# Supporting Information

## Helquat Dyes: Helicene-Like Push-Pull Systems with Large Second-Order Nonlinear Optical Responses

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## 1) Materials

Stoddart's magic mixture[1] = MeOH/$NH_4Cl$ aq (2M)/$MeNO_2$ 7:2:1

Pent-3-yn-1-yl trifluoromethanesulfonate was prepared according to a previous report[2] (from commercially available 3-pentyn-1-ol) and was then used without further purification.

Abbreviations:

DCM = dichloromethane

equiv = equivalents

$Et_3N$ = triethylamine

EtOAc = ethyl acetate

$Et_2O$ = diethyl ether

MeOH = methanol

RT = room temperature

$TfO^- = CF_3SO_3^-$

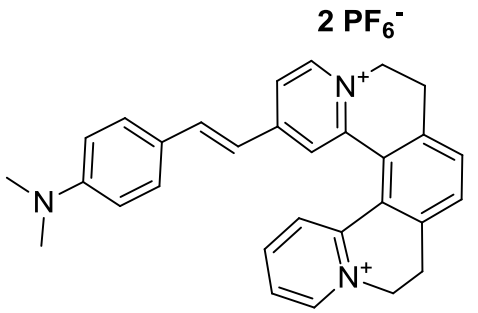
TLC = thin-layer chromatography

## 2) X-ray analysis

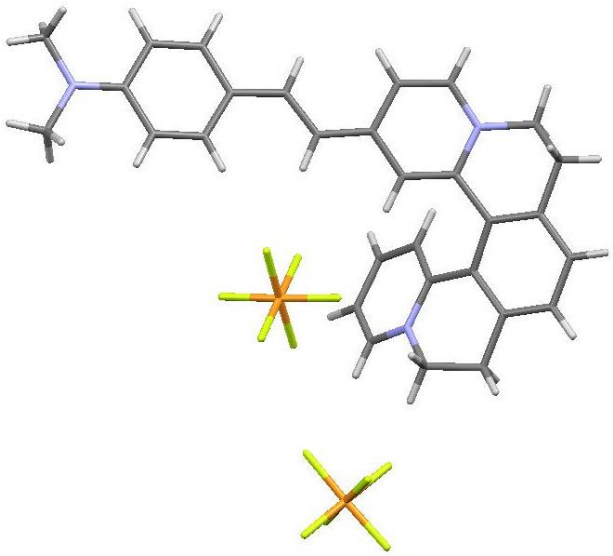
Crystallographic data were collected on a diffractometer equipped with a CCD detector using a monochromatized MoKα radiation (λ = 0.71073 Å) at a temperature of 150(2) K. The structure was solved by direct methods (SHELXS)[4] and refined by full matrix least squares based on $F^2$ (SHELXL97).[4] The hydrogen atoms on carbons were fixed into idealized positions (riding model) and assigned temperature factors either $H_{iso}$(H) = 1.2 $U_{eq}$(pivot atom) or $H_{iso}$(H) = 1.5 $U_{eq}$ for methyl moiety.

**[5]Helquat dye 1**

**CCDC 1410502**




Chemical Formula: $C_{30}H_{29}F_{12}N_3P_2$
Molecular Weight: 721.50



**Ion exchange:** [5]Helquat dye bis(triflate) **1** (22 mg, 0.030 mmol) was dissolved in water (20 mL) and $KPF_6$ (55 mg, 0.300 mmol, 10 equiv) in water (1 mL) was added. The mixture in the flask was covered with Alufoil and was stirred at RT for 3 h. The precipitate was then filtered through a sinter (porosity S3). The solid was washed twice with water (2 × 3 mL). The solid product from the sinter was collected using acetone. After volatiles were removed, [5]helquat dye bis(hexafluorophosphate) was obtained as a dark violet solid (21 mg, 97 %, 0.029 mmol).

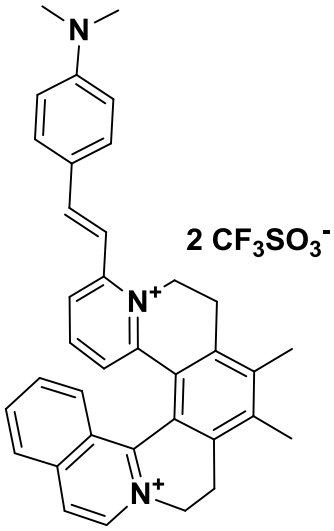
**Single crystals:** Crystals of [5]helquat dye bis(hexafluorophosphate) suitable for X-ray analysis were grown *via* slow diffusion of *t*-BuOMe into a methanolic solution of the helquat at room temperature (22–25 °C) in the dark over 8 days.

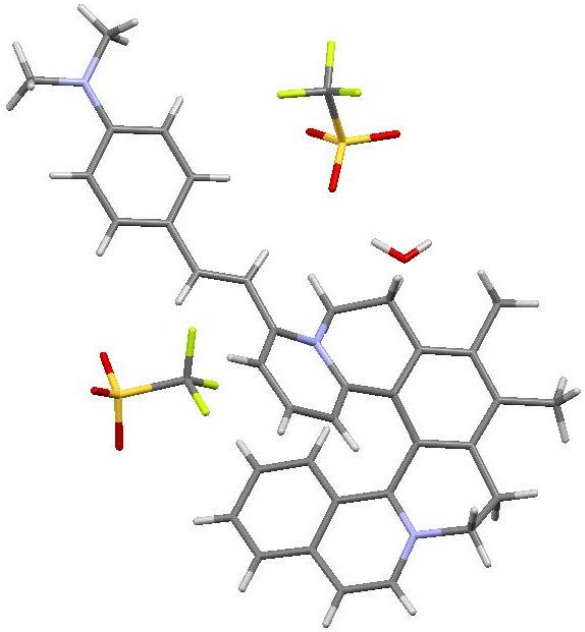
**Crystal data for CCDC 1410502:** $C_{30}H_{29}N_3$•2($F_6P$), $M_r$ = 721.50; Monoclinic, $P2_1/c$ (No 14), $a$ = 8.3850(12) Å, $b$ = 23.460(3) Å, $c$ = 15.353(2) Å, $\beta$ = 96.621(7)° , $V$ = 2999.9(7) Å$^3$ , Z = 4, $D_x$ = 1.597 Mg m$^{-3}$, green prism of dimensions 0.51 × 0.37 × 0.35 mm, multi-scan absorption correction ($\mu$ = 0.25 mm$^{-1}$), $T_{min}$ = 0.885, $T_{max}$ = 0.919; a total of 48987 measured

reflections ($\theta_{max}$= 27.5˚), from which 6878 were unique ($R_{int}$ = 0.023) and 5749 observed according to the $I > 2\sigma(I)$ criterion. The refinement converged ($\Delta/\sigma_{max}$= 0.007) to $R$ = 0.053 for observed reflections and $wR(F^2)$ = 0.158, GOF = 1.04 for 426 parameters and all 6878 reflections. The final difference Fourier map displayed no peaks of chemical significance. ($\Delta\rho_{max}$ = 1.01, $\Delta\rho_{min}$ = –0.55 eÅ$^{-3}$).

**[6]Helquat dye 6**

**CCDC 1012247**



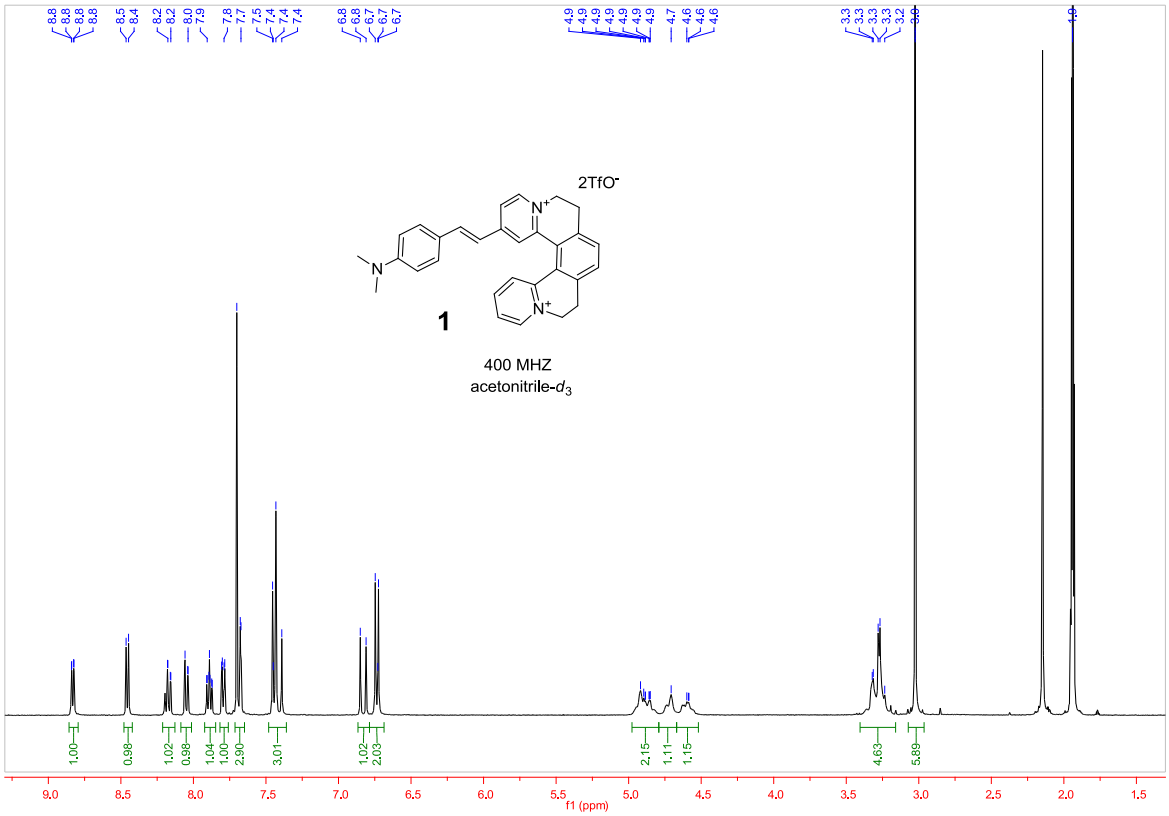
Chemical Formula: $C_{38}H_{35}F_6N_3O_6S_2$
Molecular Weight: 807.82

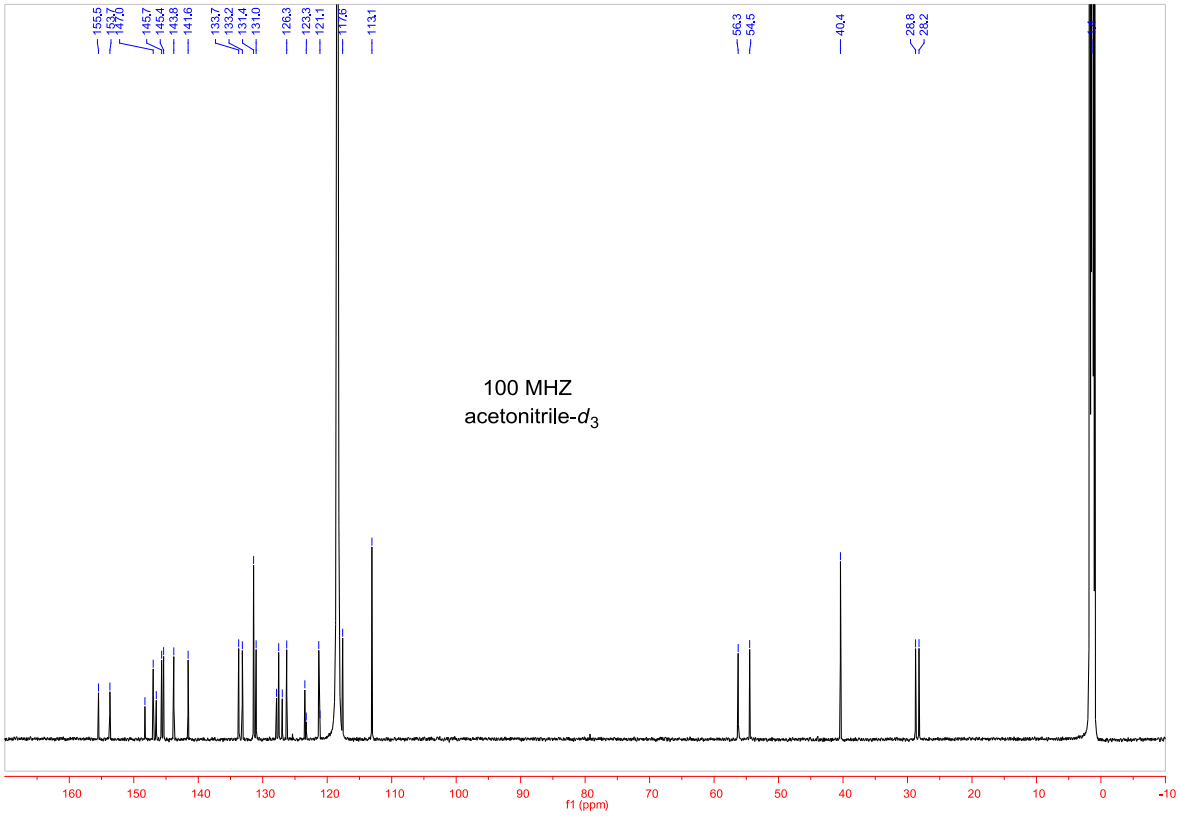
[6]Helquat dye **6** (2 mg) was dissolved in acetone (0.2 mL). Single crystals suitable for X-ray analysis were grown *via* slow diffusion of *i*-$Pr_2O$ into the solution at room temperature (22–25 °C) in the dark over 10 days.

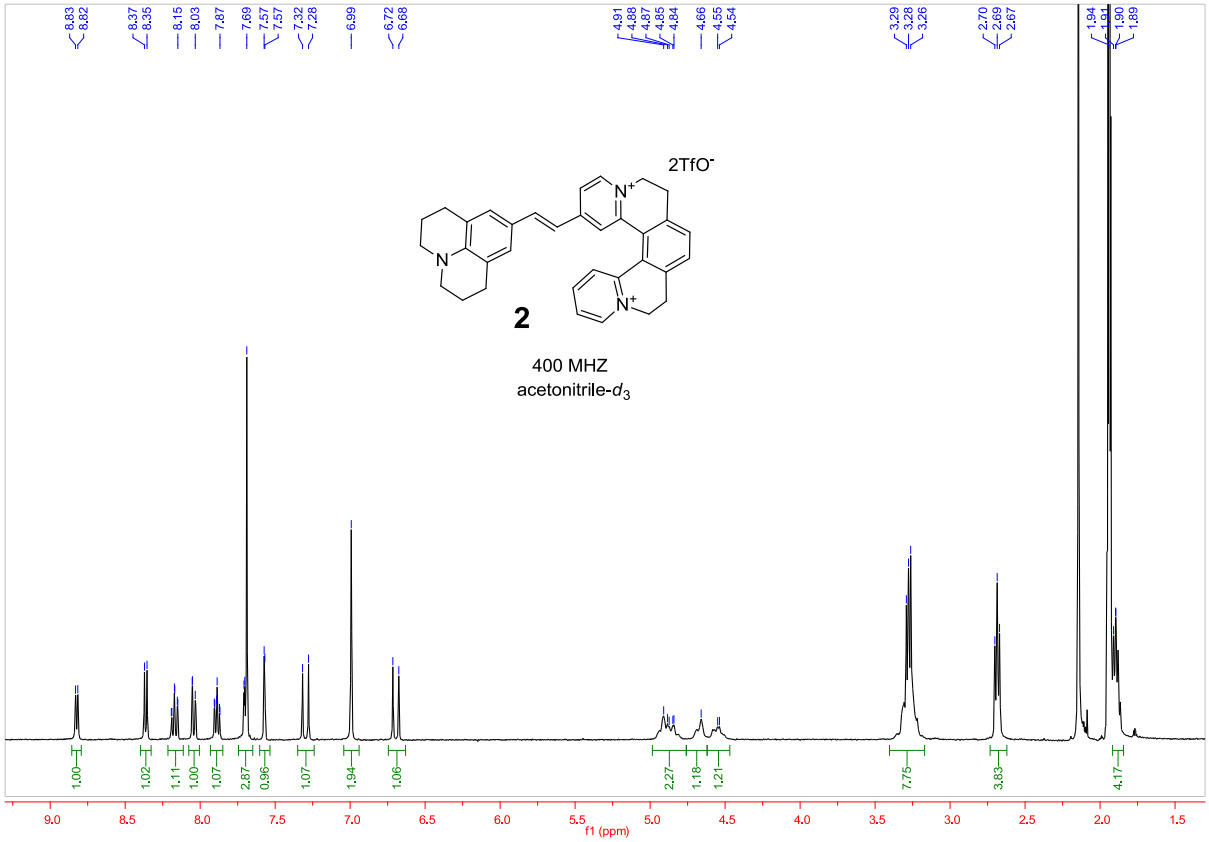
**Crystal data for CCDC 1012247:** $2(C_{36}H_{35}N_3)\bullet4(CF_3O_3S)\bullet H_2O$, $M_r$ = 1633.64; Triclinic, *P*1 (No 1), $a$ = = 9.7985(3) Å, $b$ = 10.1396(4) Å, $c$ = 19.4403(7) Å, $\alpha$ = 89.593(1)°, $\beta$ = 83.894(1)° , $\gamma$ = 68.851(1) °, $V$ = 1790.12(11) Å$^3$ , Z = 1, $D_x$ = 1.515 Mg m$^{-3}$, red plate of dimensions 0.51 × 0.43 × 0.17 mm, multi-scan absorption correction ($\mu$ = 0.24 mm$^{-1}$) $T_{min}$ = 0.890, $T_{max}$ = 0.962; a total of 44178 measured reflections ($\theta_{max}$= 27.5˚), from which 16387 were unique ($R_{int}$ = 0.026) and 14165 observed according to the $I > 2\sigma(I)$ criterion. The refinement converged ($\Delta/\sigma_{max}$= 0.001) to $R$ = 0.071 for observed reflections and $wR(F^2)$ = 0.201, GOF = 1.01 for 1001 parameters and all 16387 reflections. The final difference Fourier map displayed no peaks of chemical significance; positive ones are in the vicinity of the triflate moiety, due to its disorder ($\Delta\rho_{max}$ = 1.70, $\Delta\rho_{min}$ = –0.61 eÅ$^{-3}$).

The structure was refined in the noncentrosymmetric space group *P*1, however two helquat cations follow closely the centrosymmetric space group *P*-1 (both enantiomers are present). In this space group, the triflate anions would appeared to be vastly disordered, therefore low symmetry was selected for final refinement. One isolated peak of positive electron density was assigned to a water molecule, but its hydrogen atoms could not be found on the difference map and were therefore placed in positions suitable for hydrogen bonds.

# 3) $^{1}$H and $^{13}$C NMR spectra

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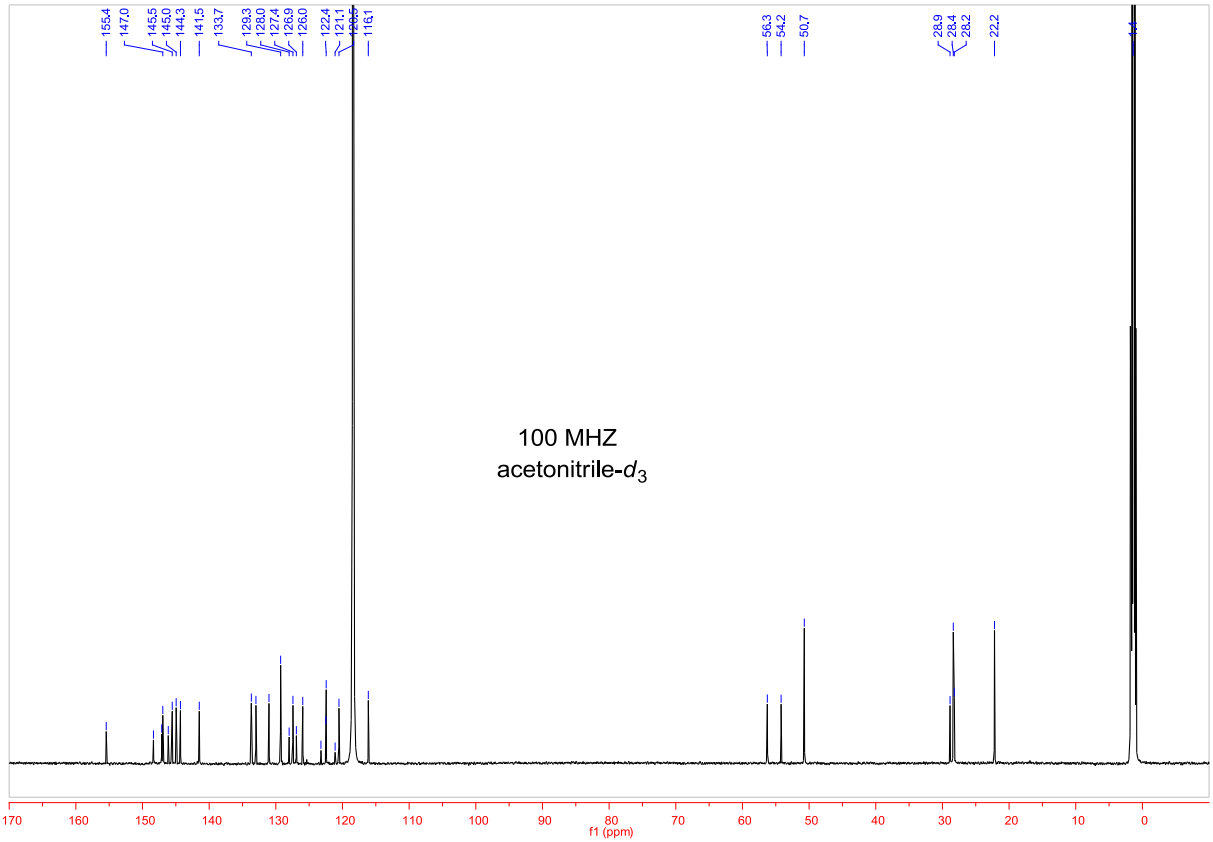
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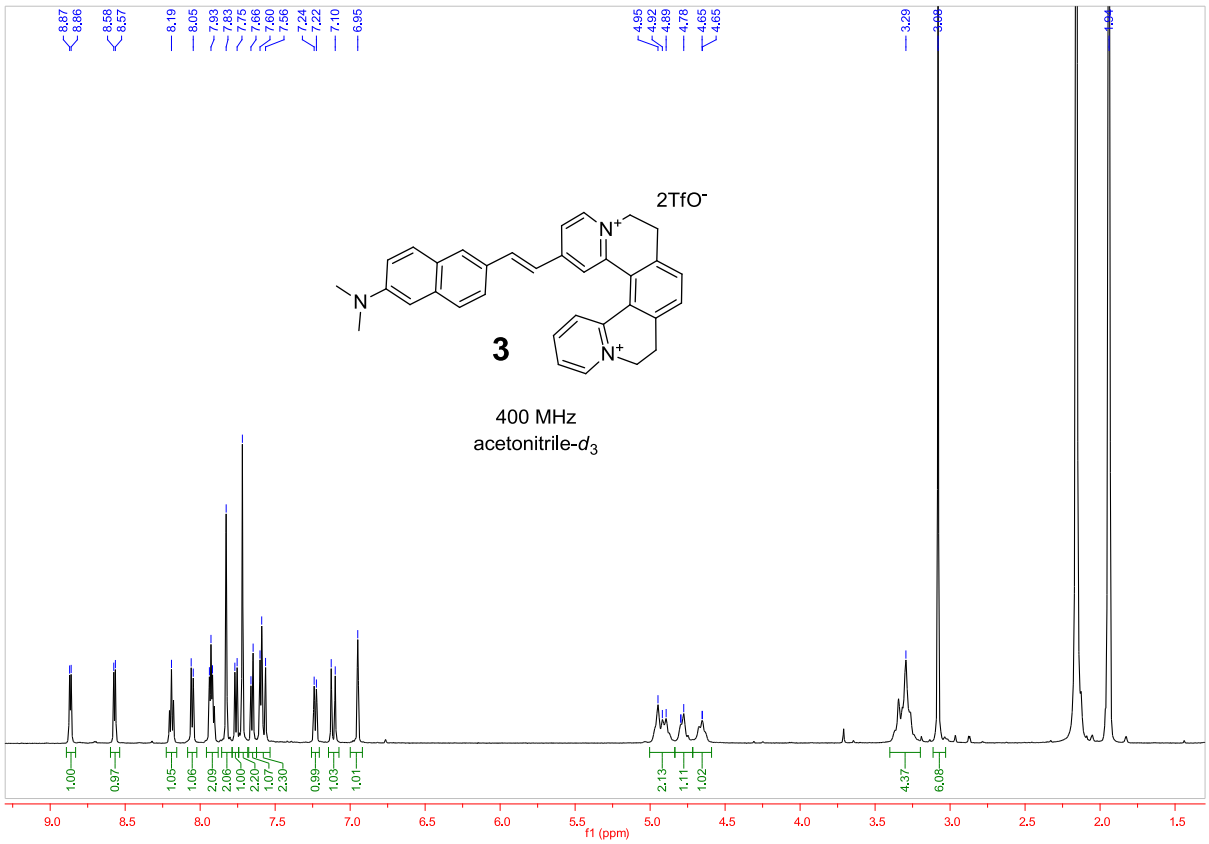
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4.65
4.65
3.29
3.09
1.94
2TfO-
N+
N
N+
3
400 MHz
acetonitrile-d3
1.00
0.97
1.05
1.06
2.09
2.06
1.00
2.20
1.07
2.30
0.99
1.03
1.01
2.13
1.11
1.02
4.37
6.08
9.0
8.5
8.0
7.5
7.0
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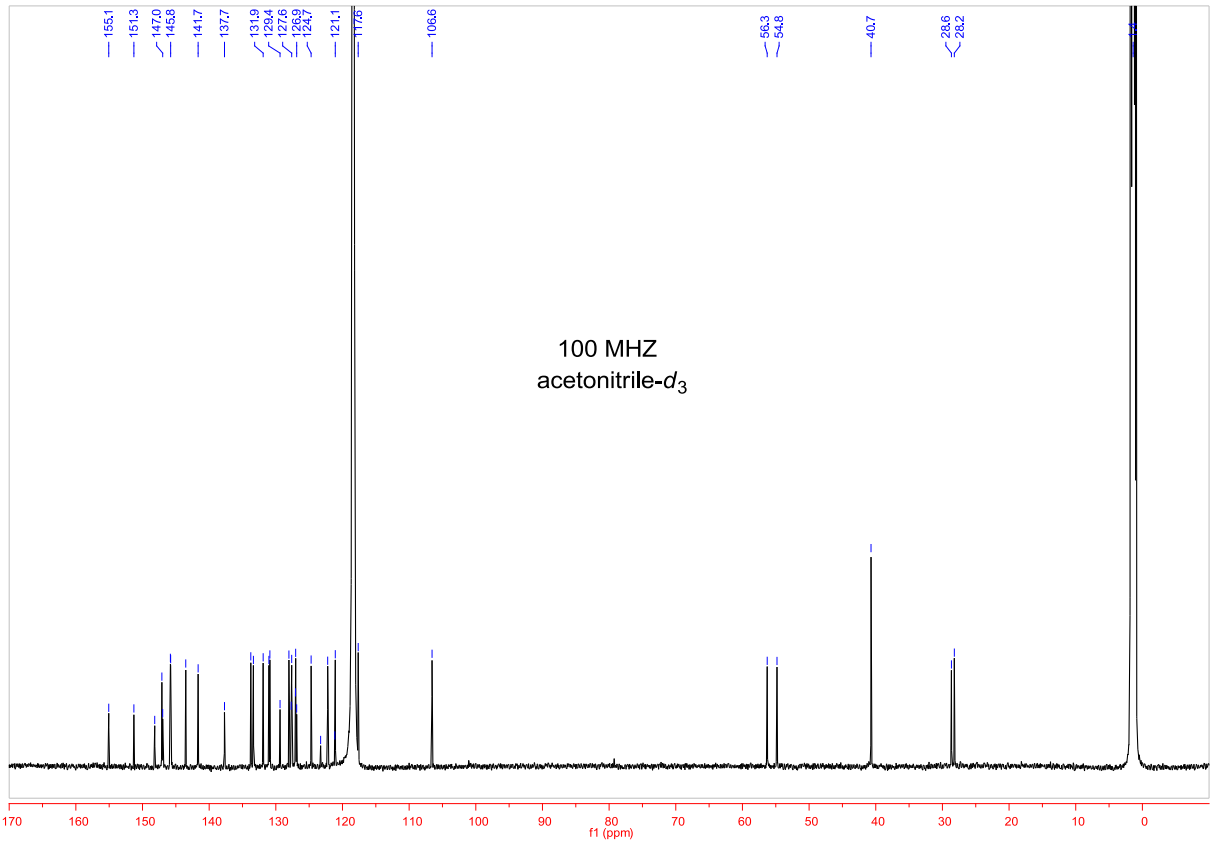
f1 (ppm)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141.7
137.7
131.9
128.4
127.6
127.2
124.7
121.1
117.8
106.6
56.3
54.8
40.7
28.6
28.2
100 MHZ
acetonitrile-d3
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150
140
130
120
110
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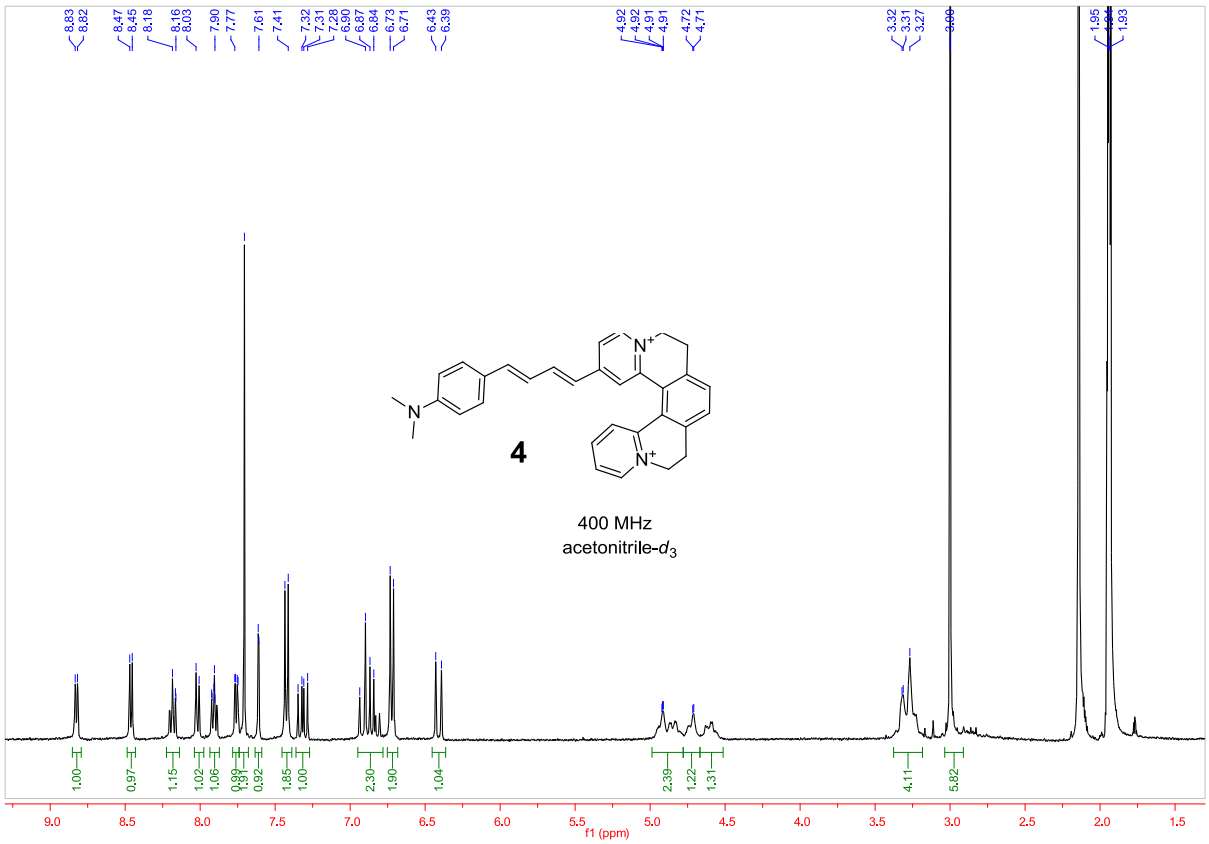
70
60
50
40
30
20
10
0
f1 (ppm)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4.71
3.32
3.31
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1.93
1.00
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1.15
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1.00
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1.90
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2.39
1.22
1.31
4.11
5.82
9.0
8.5
8.0
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4.5
4.0
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N+
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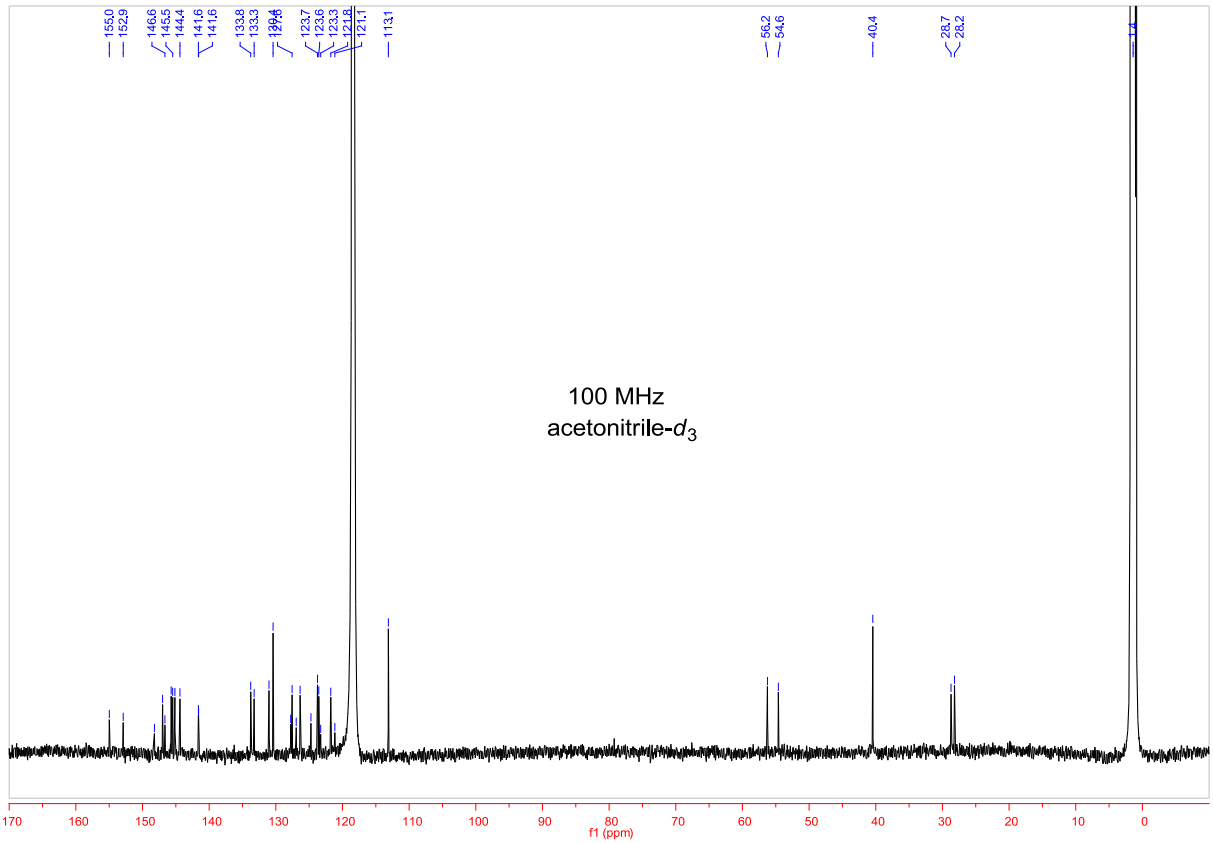
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133.3
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123.6
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121.8
121.1
113.1
56.2
54.6
40.4
28.7
28.2
100 MHz
acetonitrile-$d_3$
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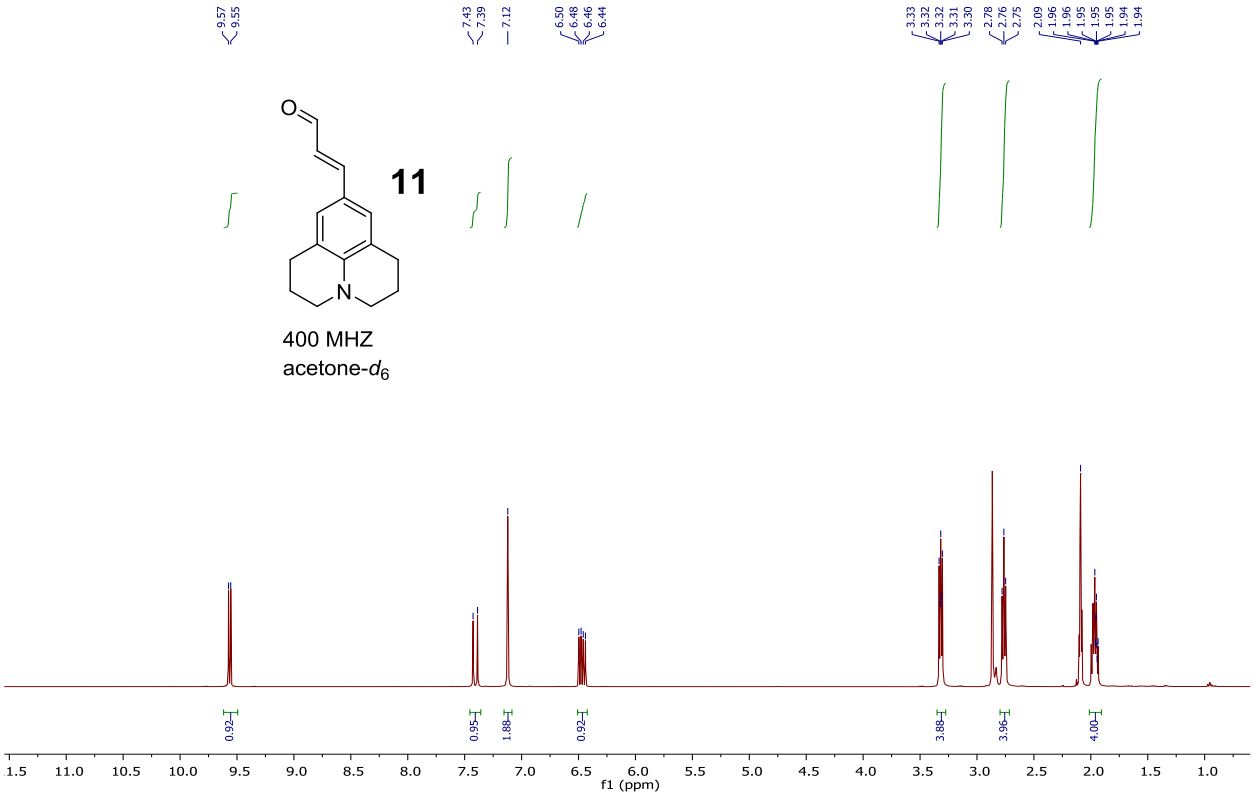
f1 (ppm)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1.96
1.95
1.95
1.95
1.94
1.94
O
11
N
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acetone-d6
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0.95
1.88
0.92
3.88
3.96
4.00
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
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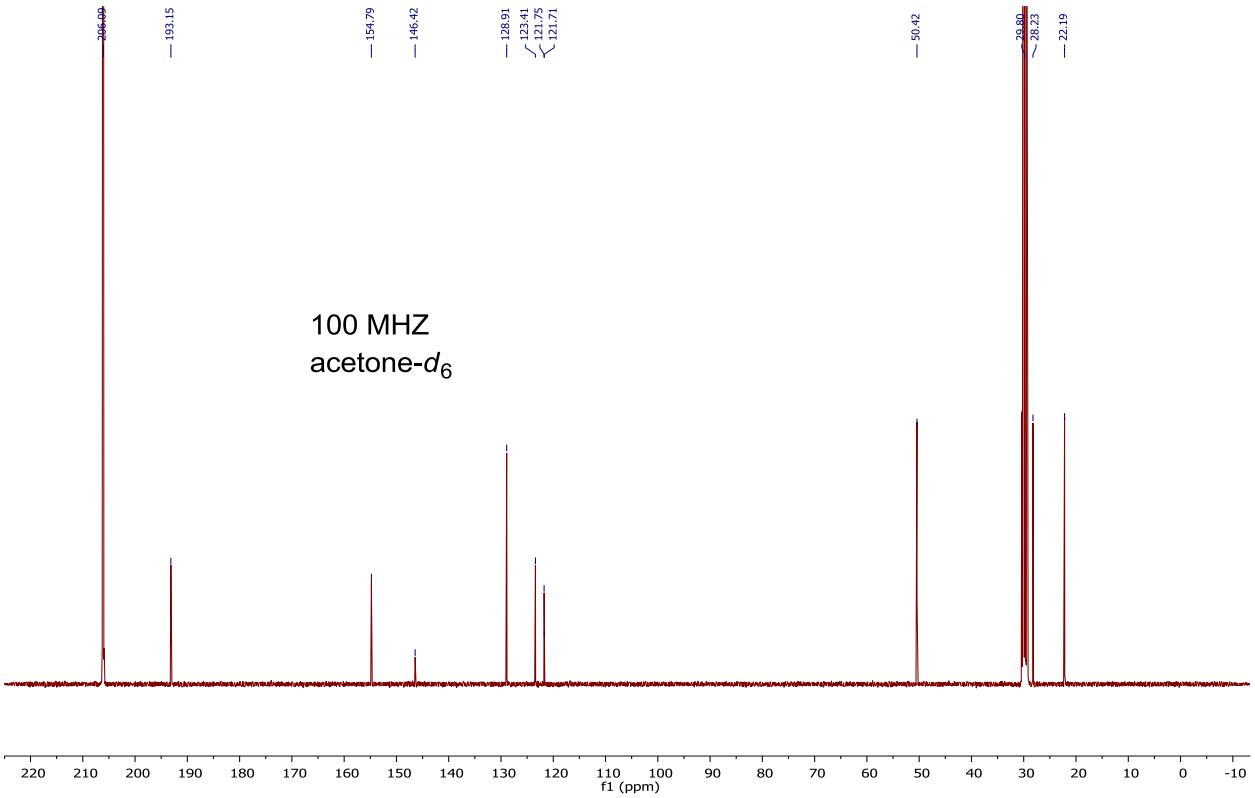
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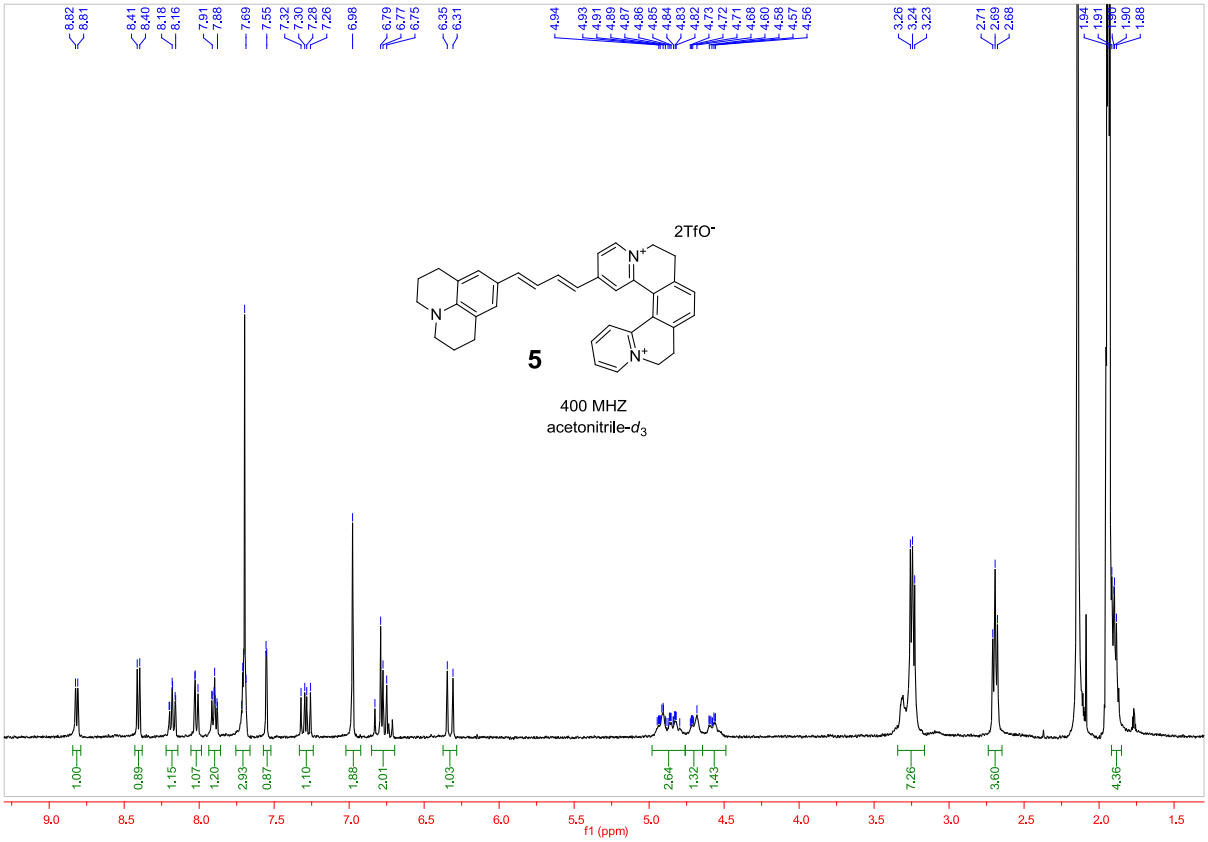
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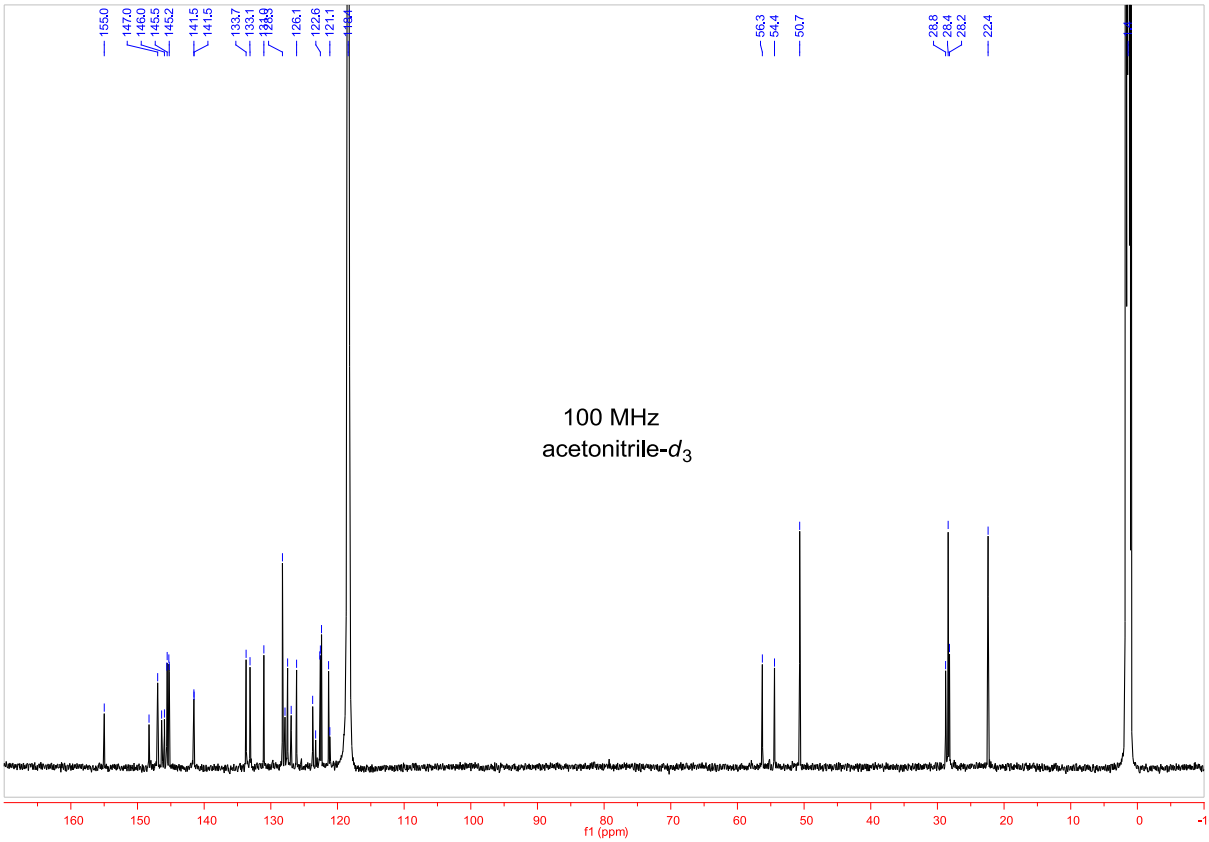
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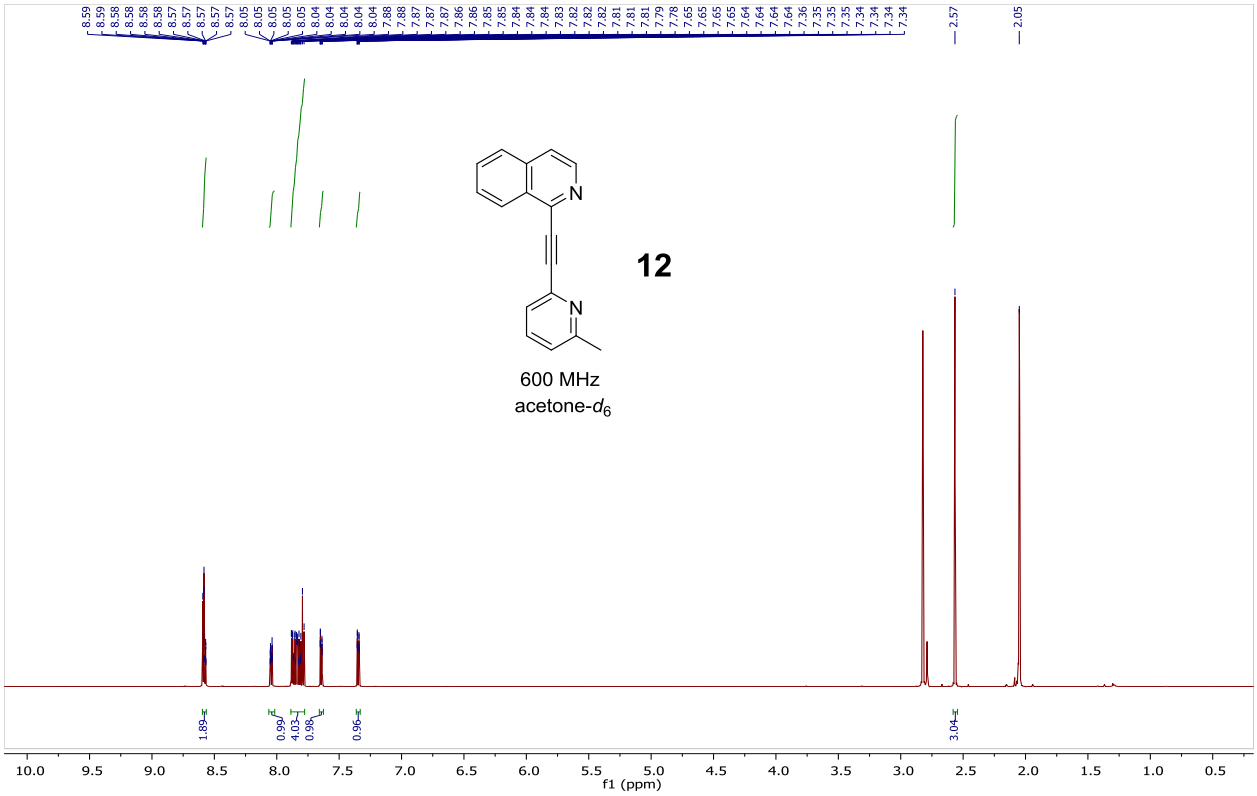
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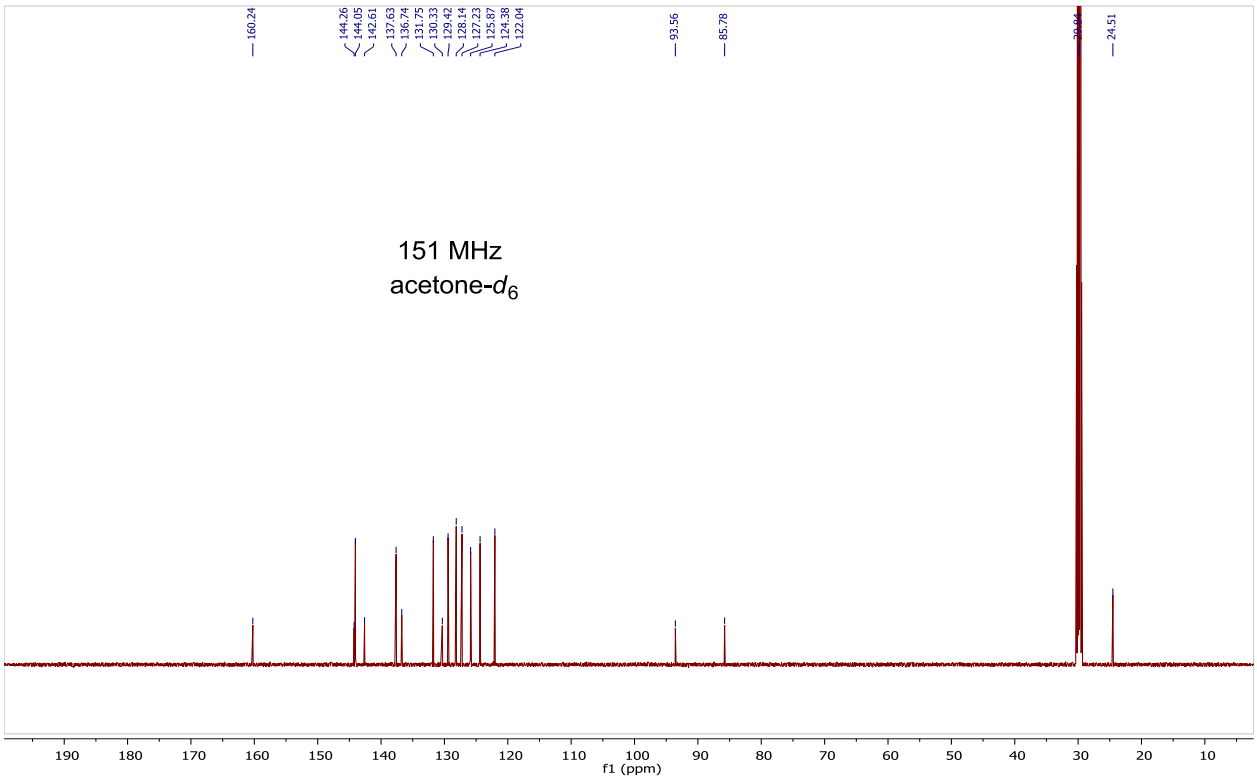
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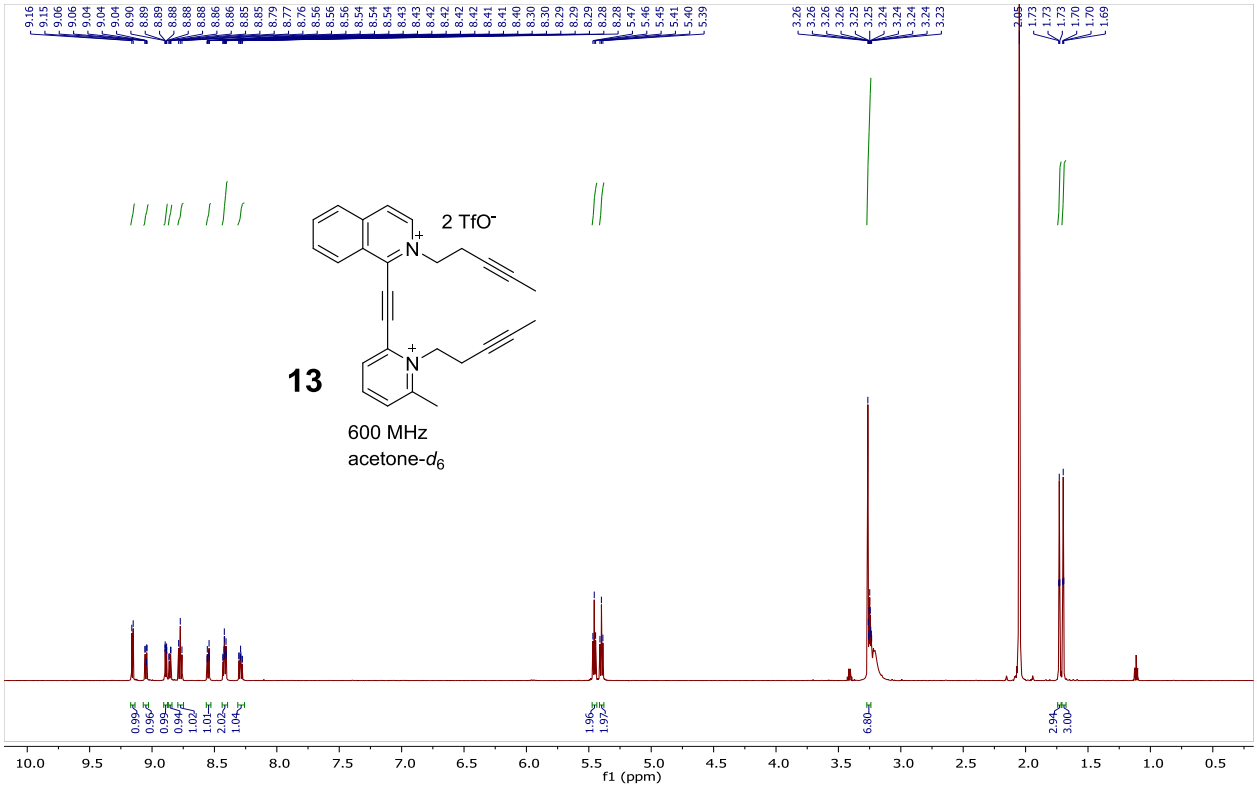
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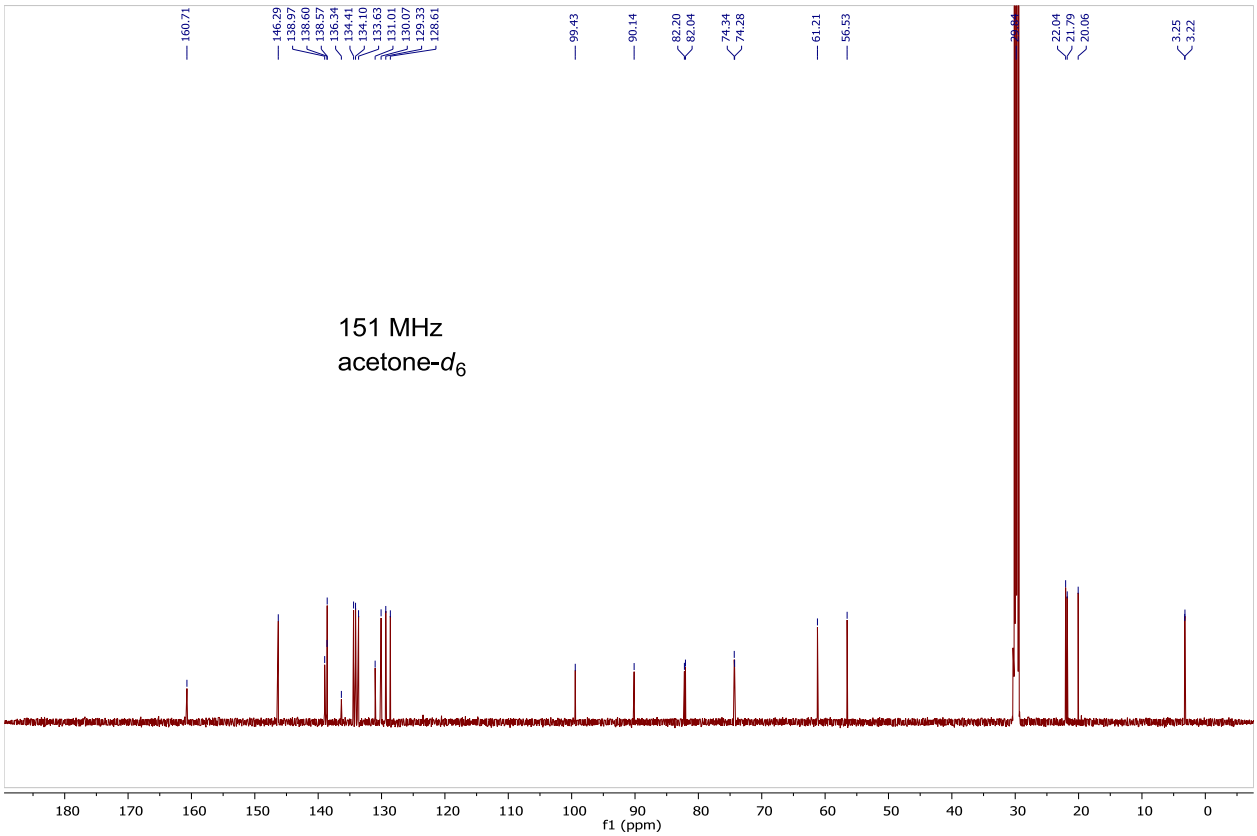
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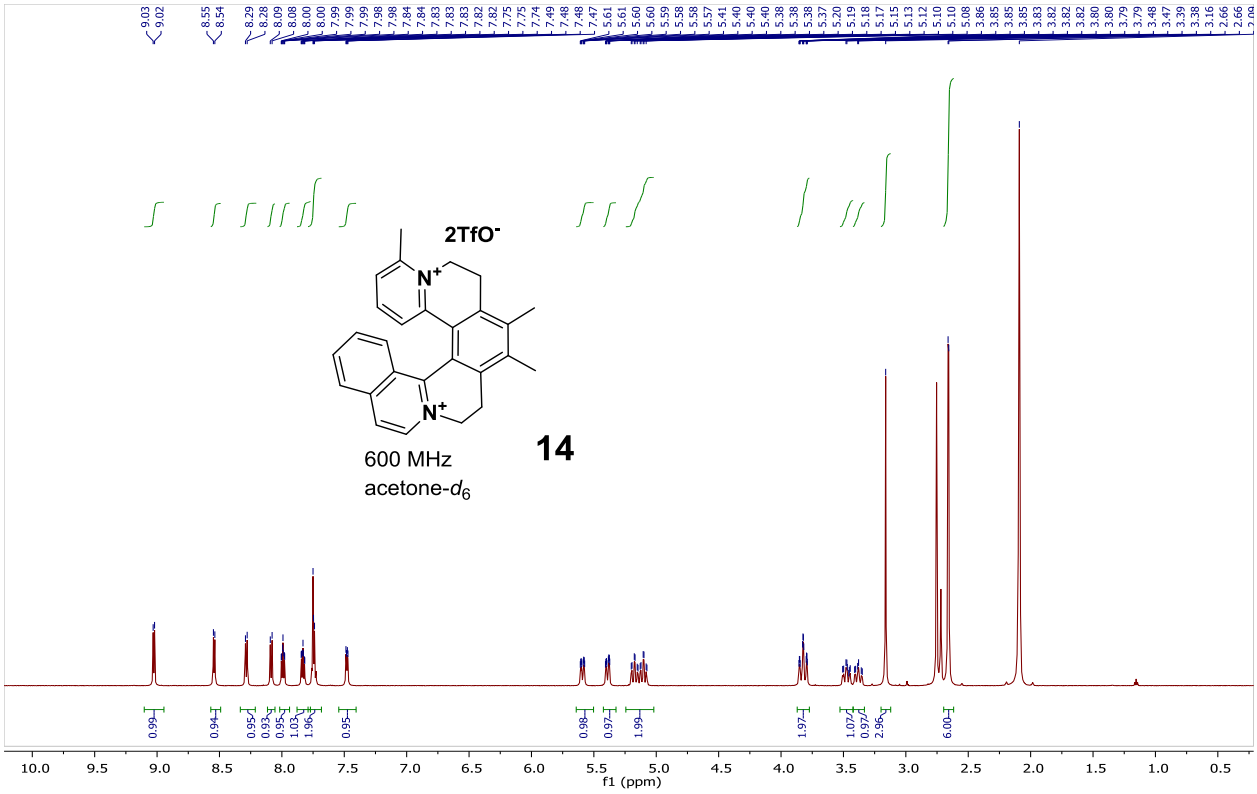
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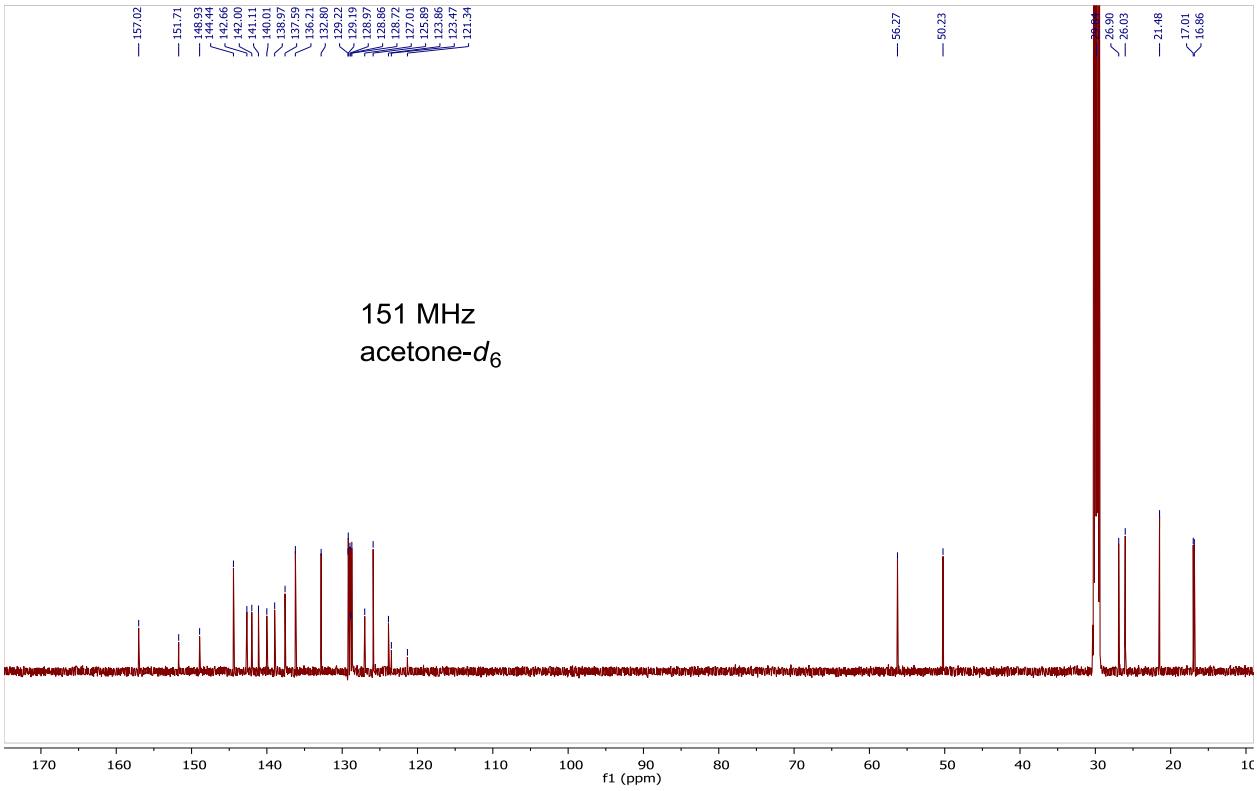
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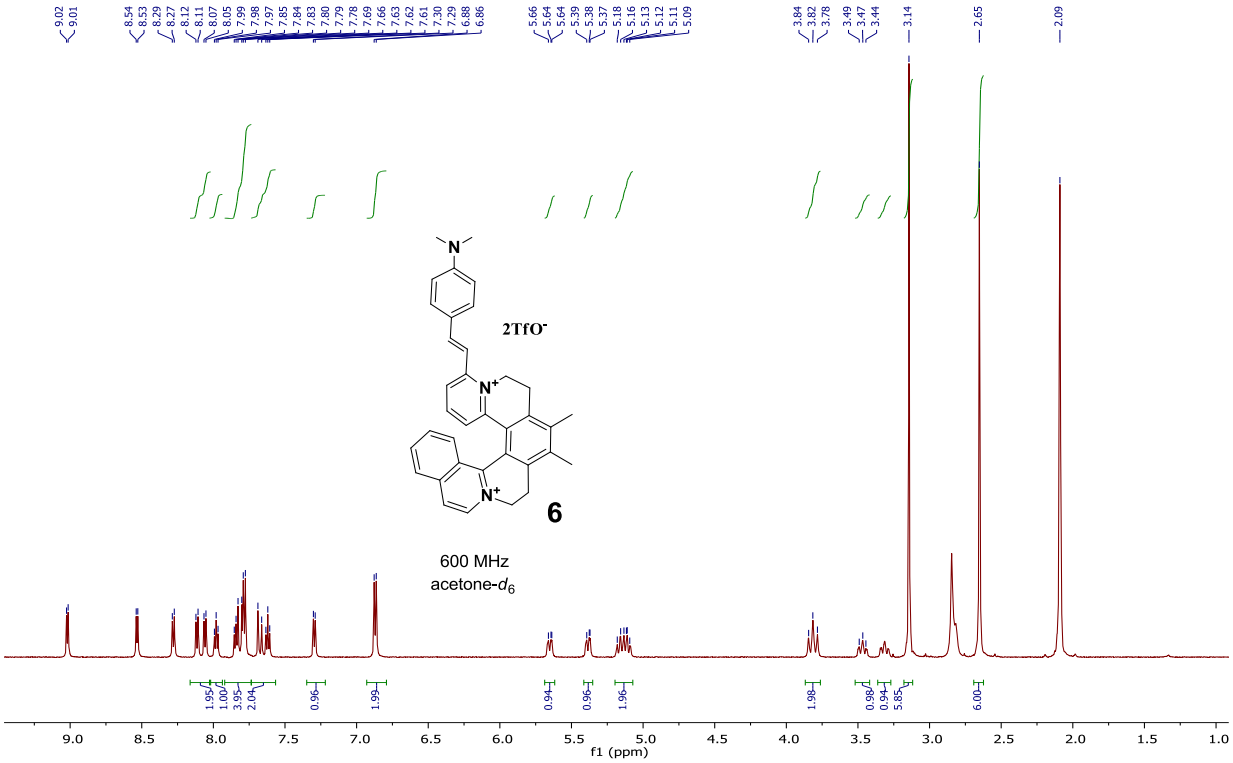
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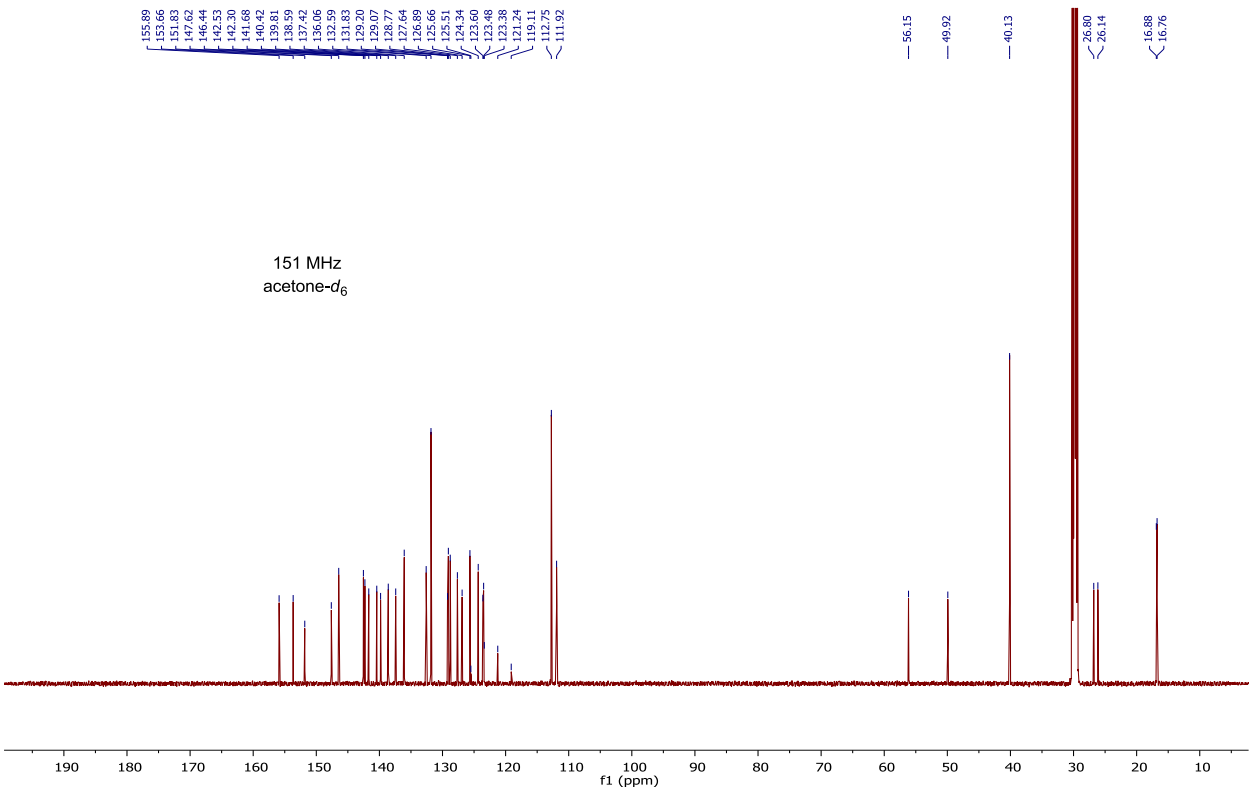
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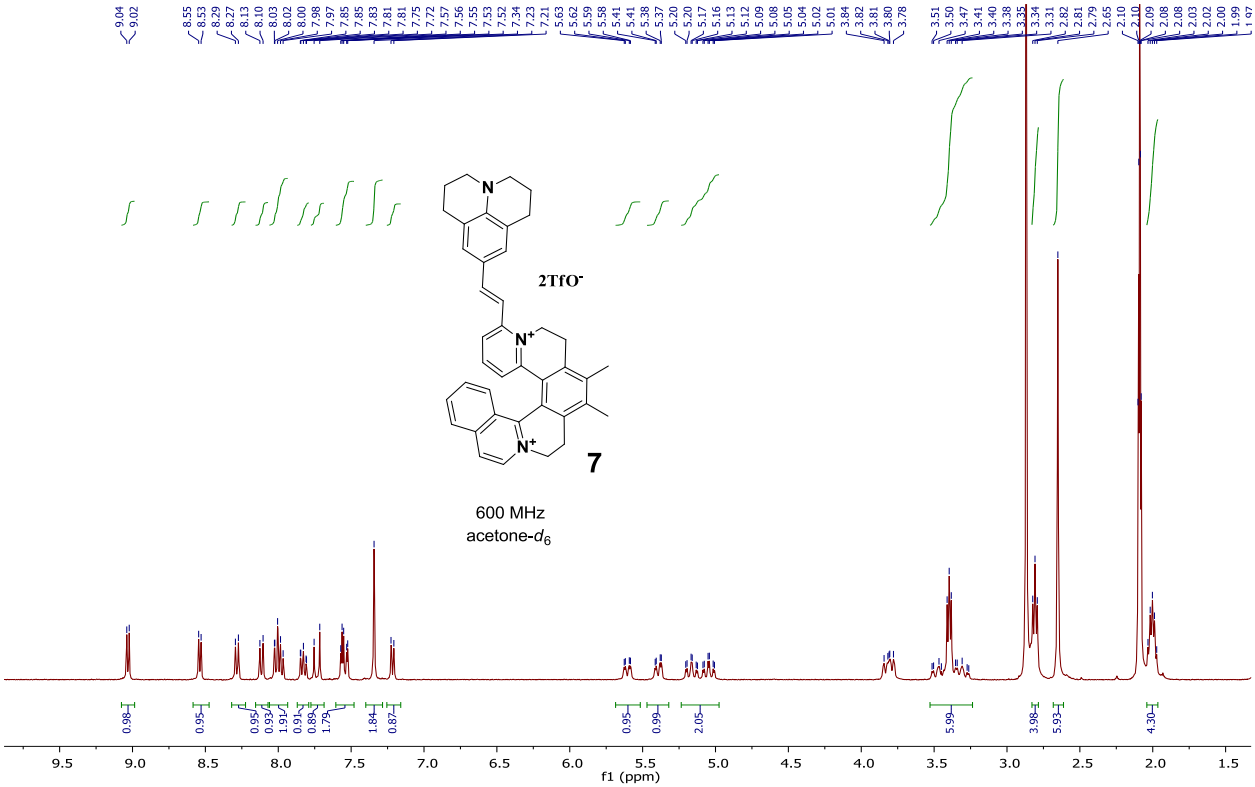
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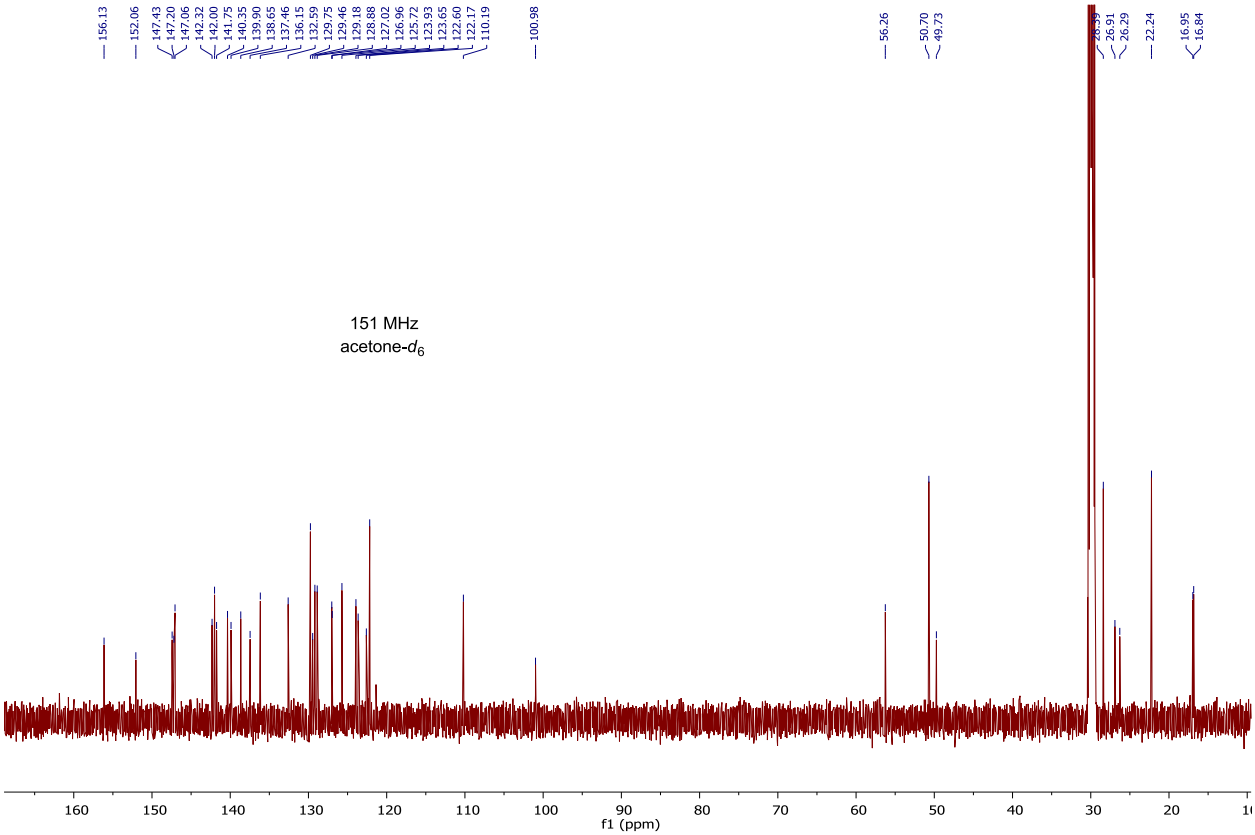
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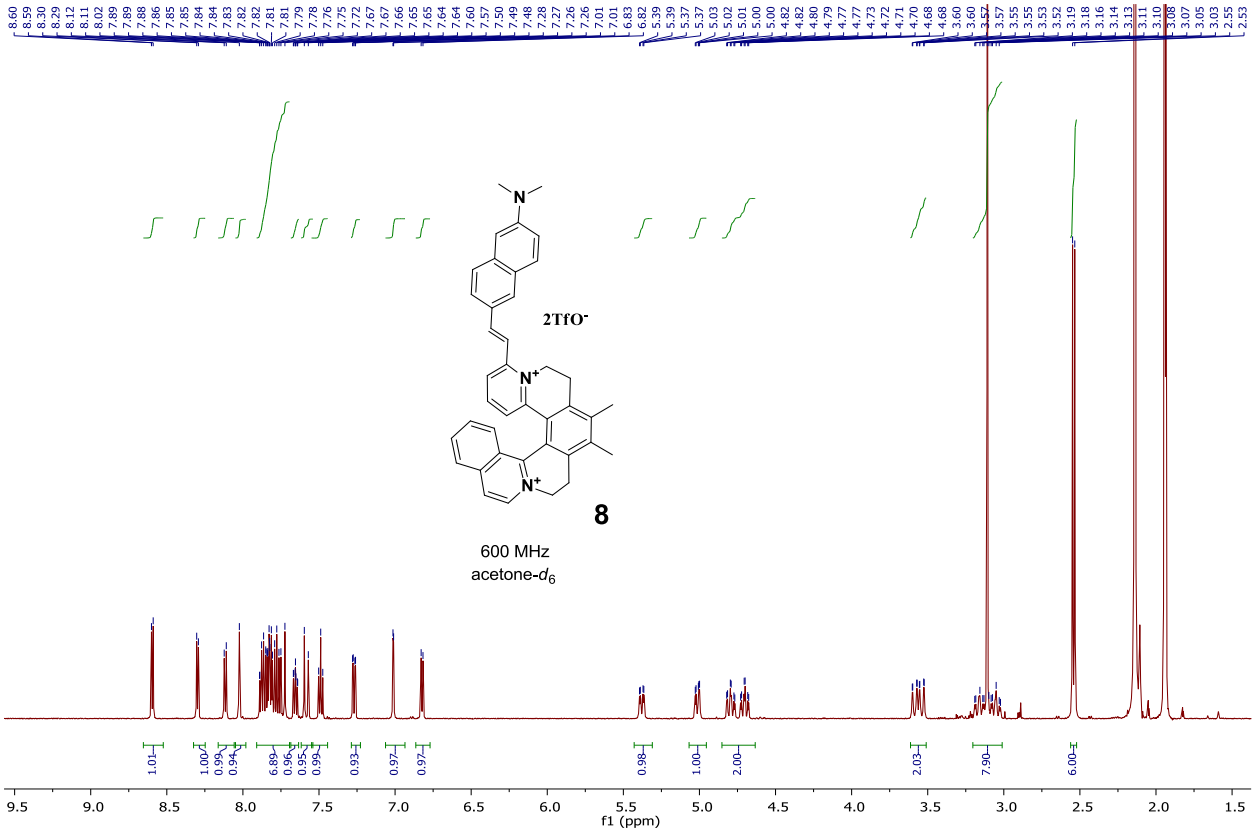
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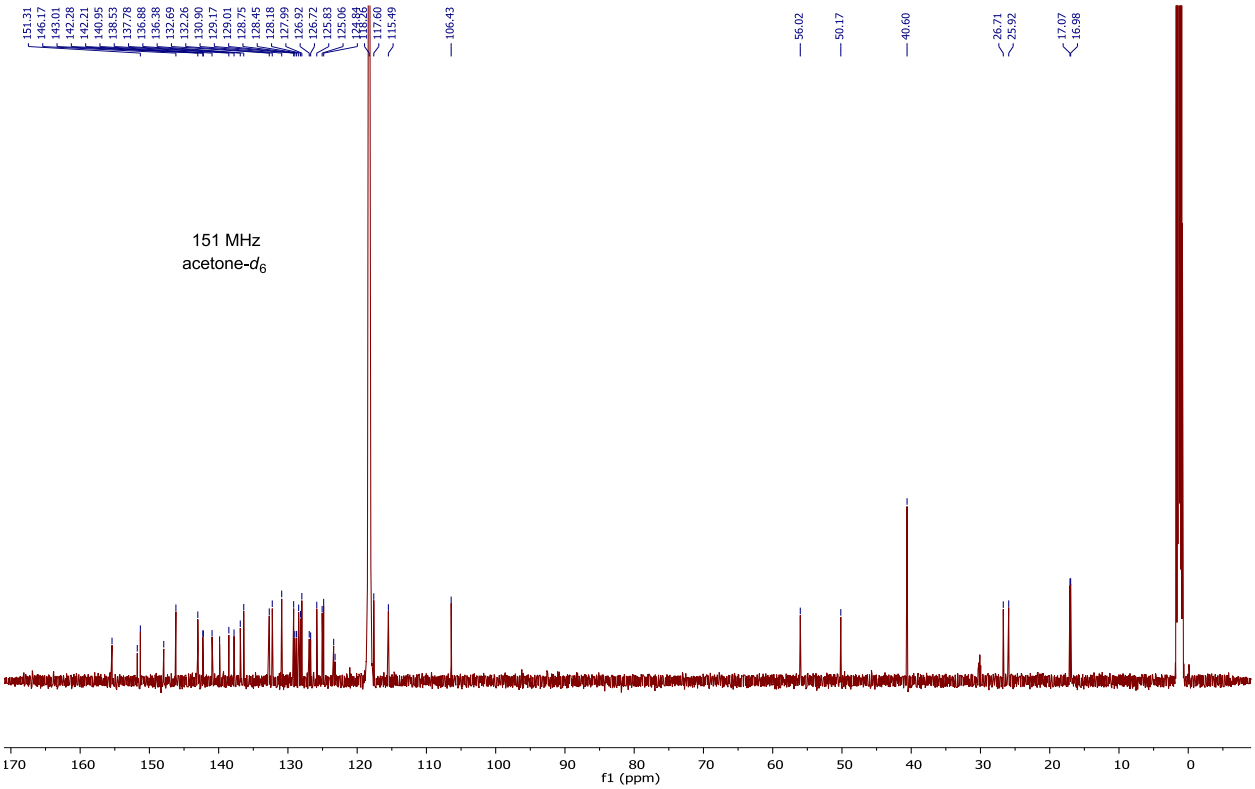
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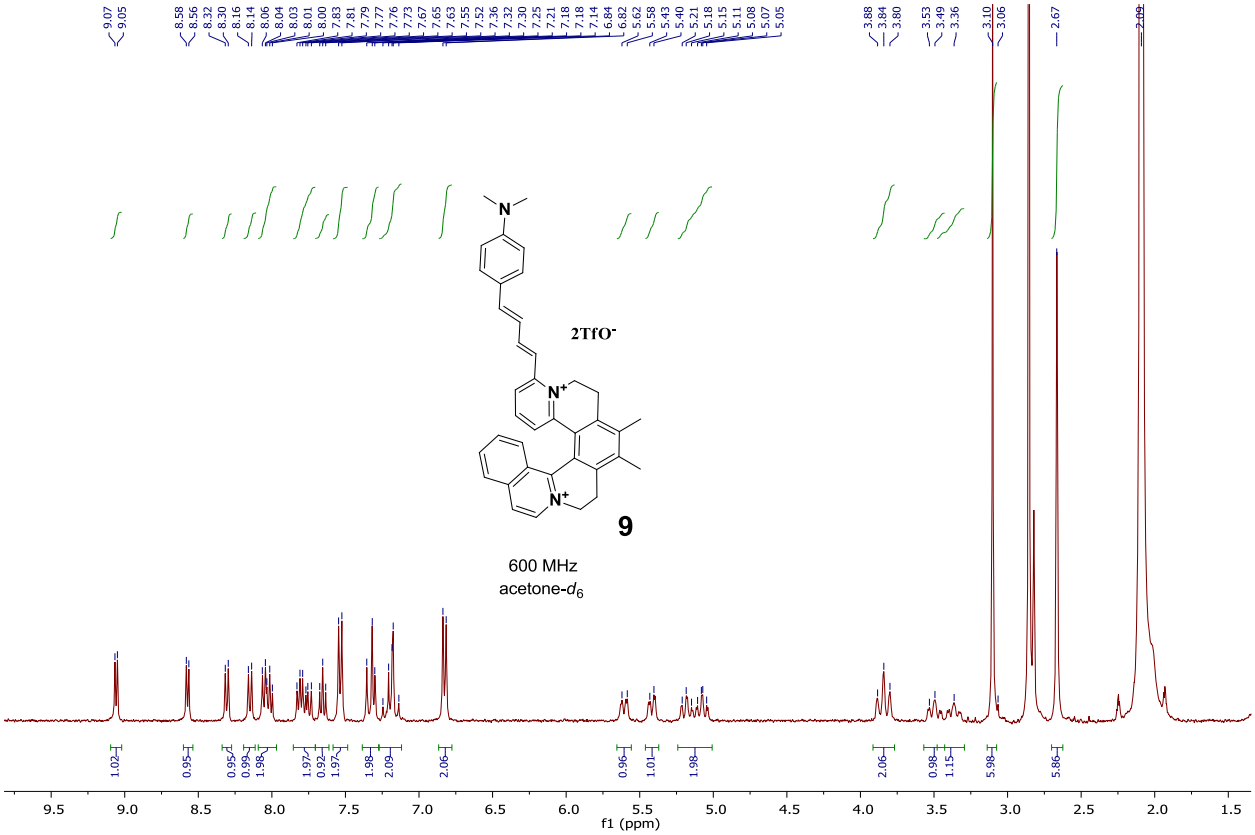
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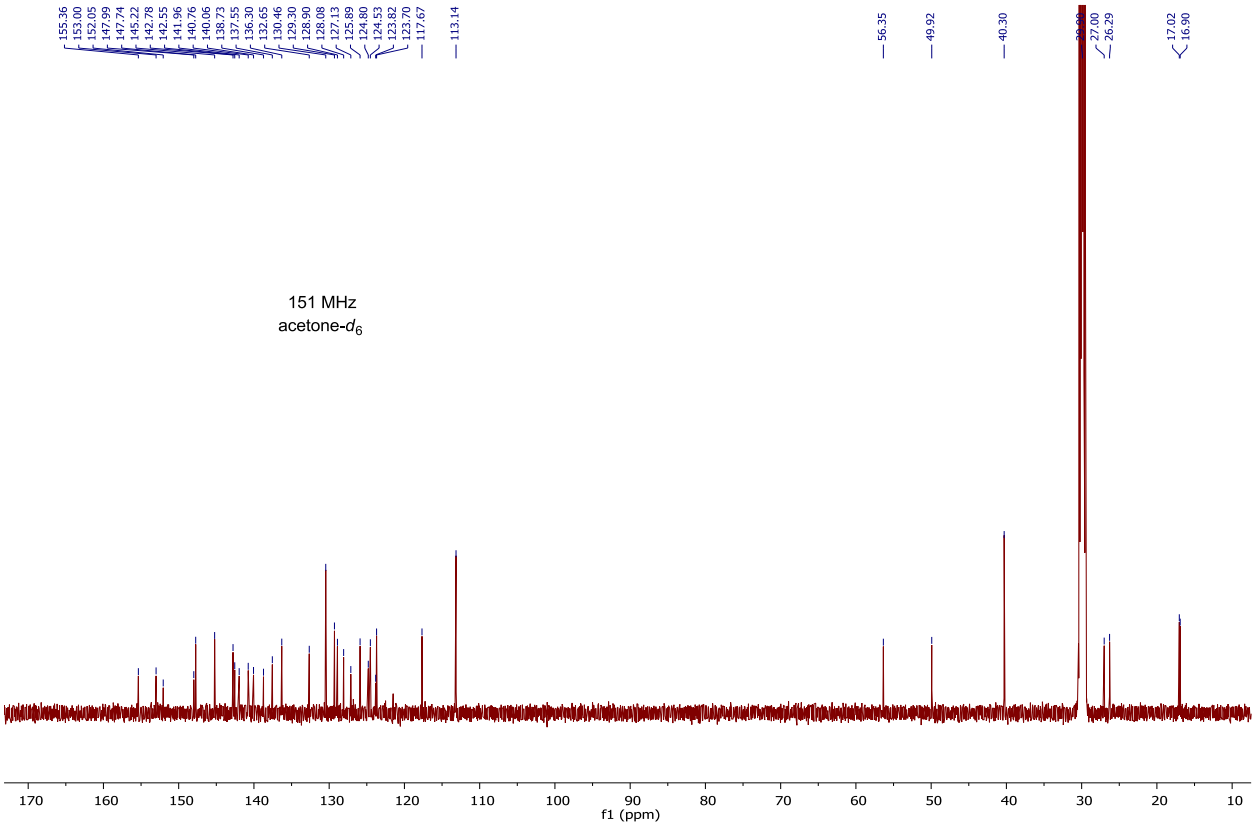
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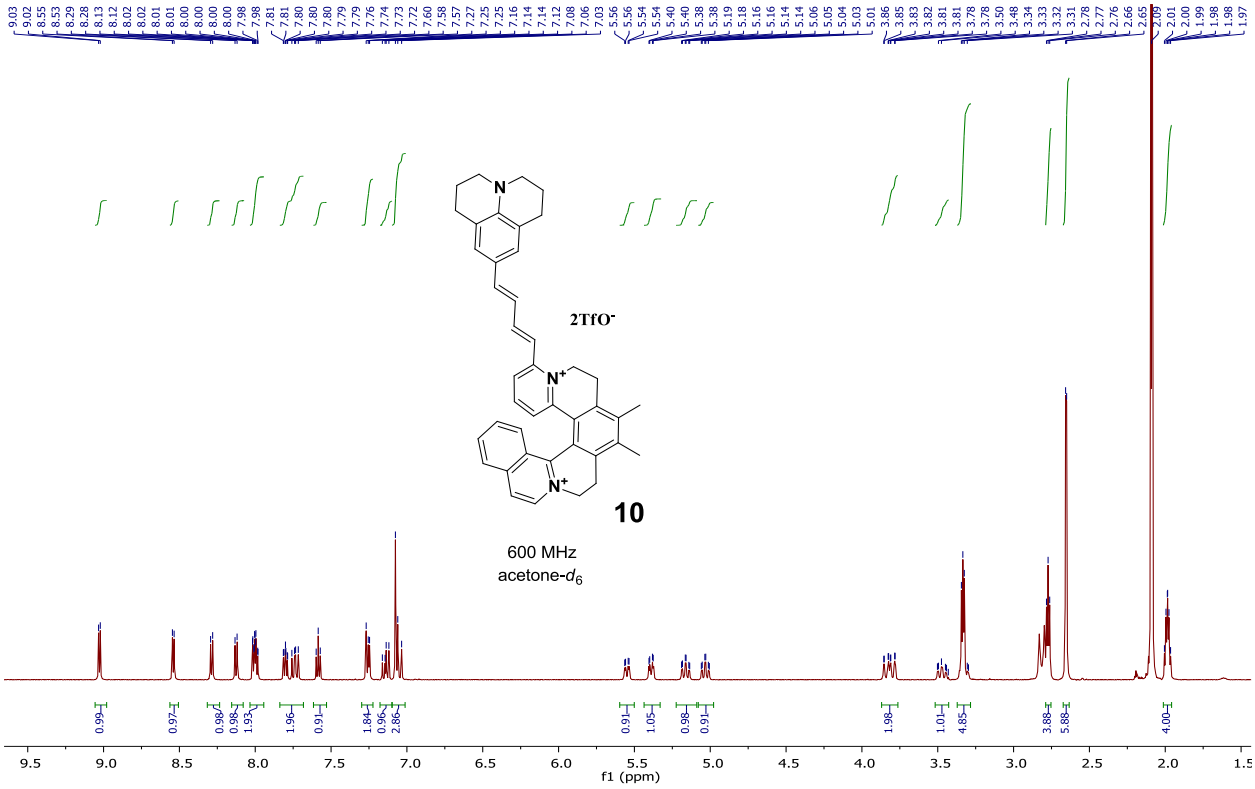
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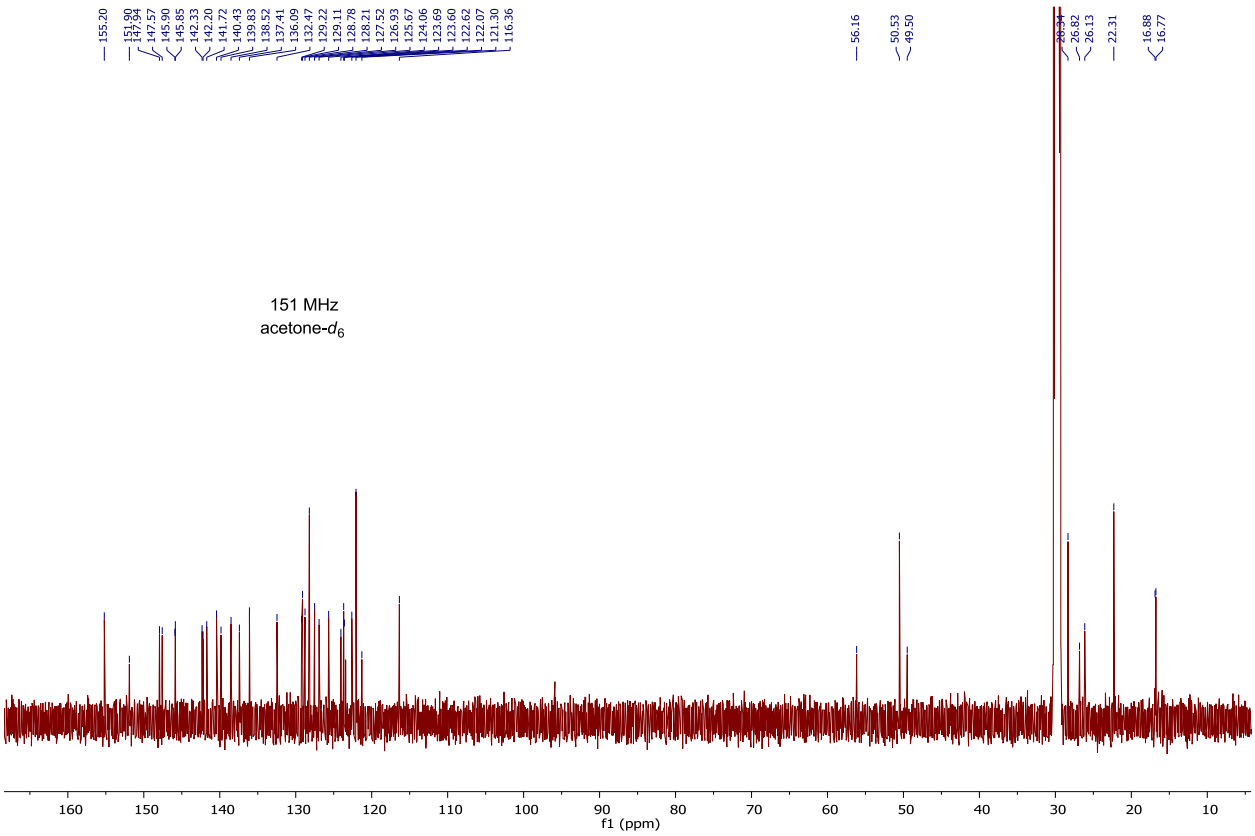
acetone-$d_6$
f1 (ppm)


151 MHz
acetone-$d_6$
f1 (ppm)

## 4) Theoretical Studies

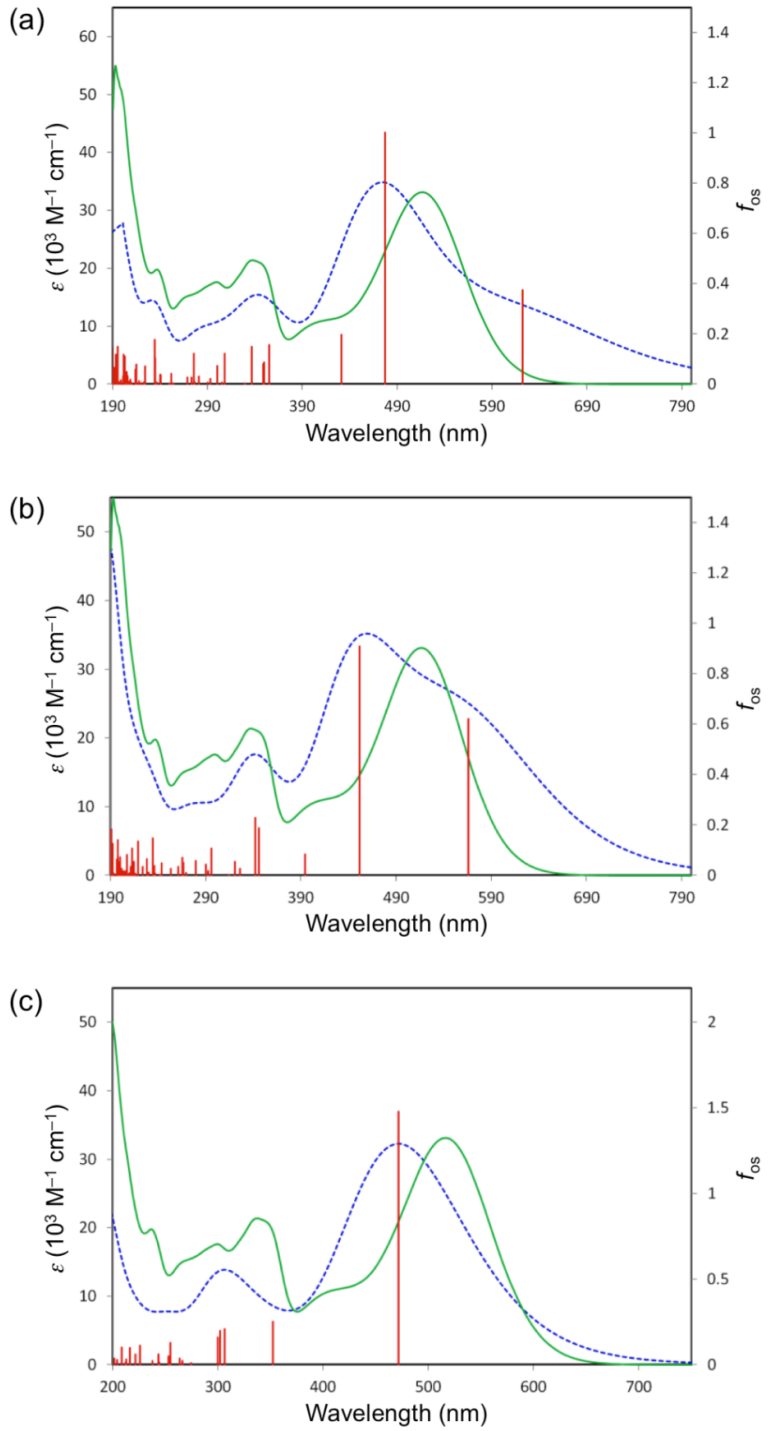



**Fig. S1.** DFT-calculated[5] (blue) and experimental (green) UV–vis absorption spectra of **1′** in MeCN, obtained by using the 6-311G(d) basis set with the functional B3LYP (a), M06 (b) or CAM-B3LYP (c). The $\varepsilon$-axes refer to the experimental data only (for the $OTf^-$ salt) and the vertical axes of the calculated data are scaled to match the main experimental absorptions. The oscillator strength axes refer to the individual calculated transitions (red).

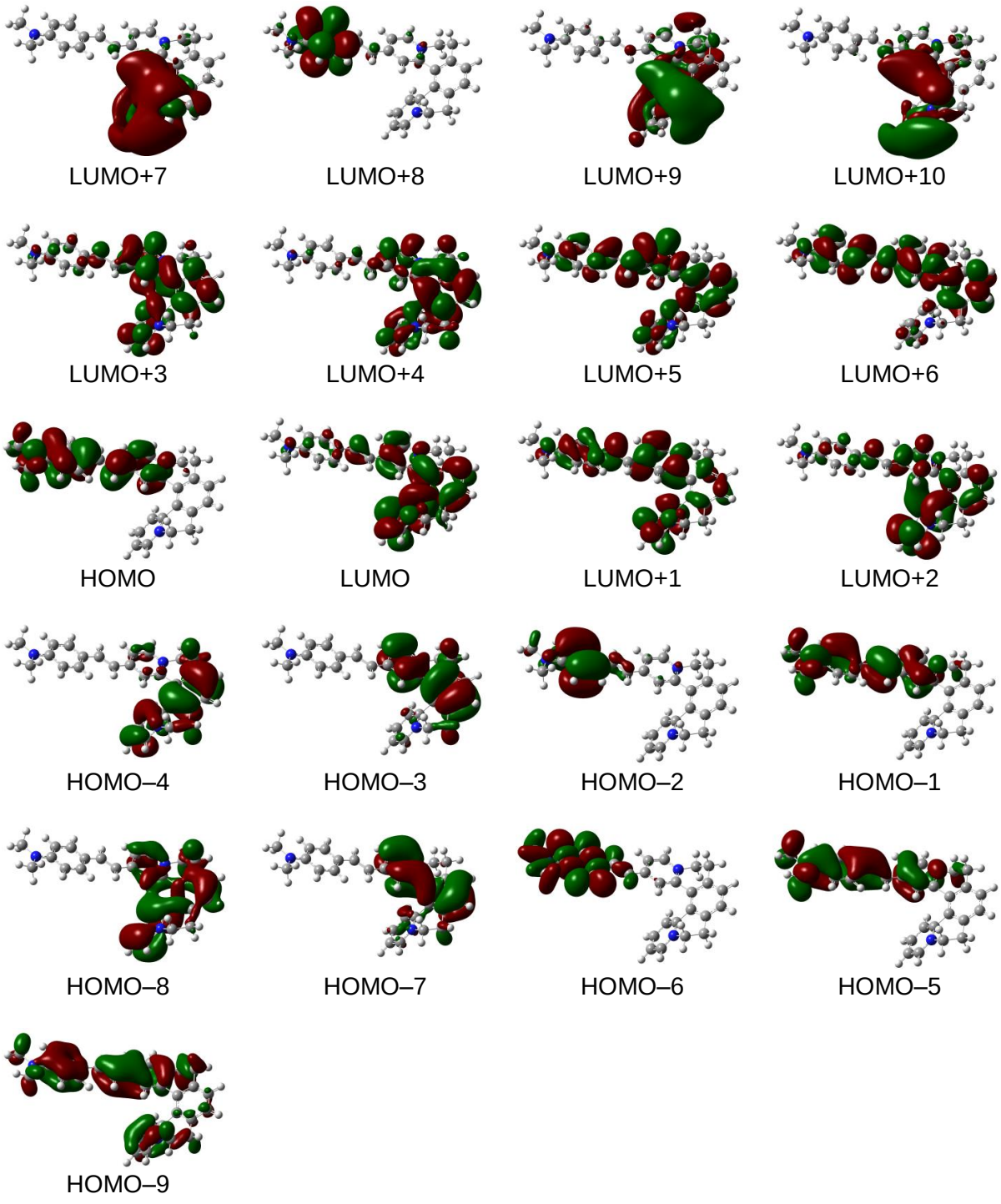



**Fig. S2.** CAM-B3LYP/6-311G(d)-derived contour surface diagrams of the frontier MOs for cation **1′** (isosurface value 0.03 au).

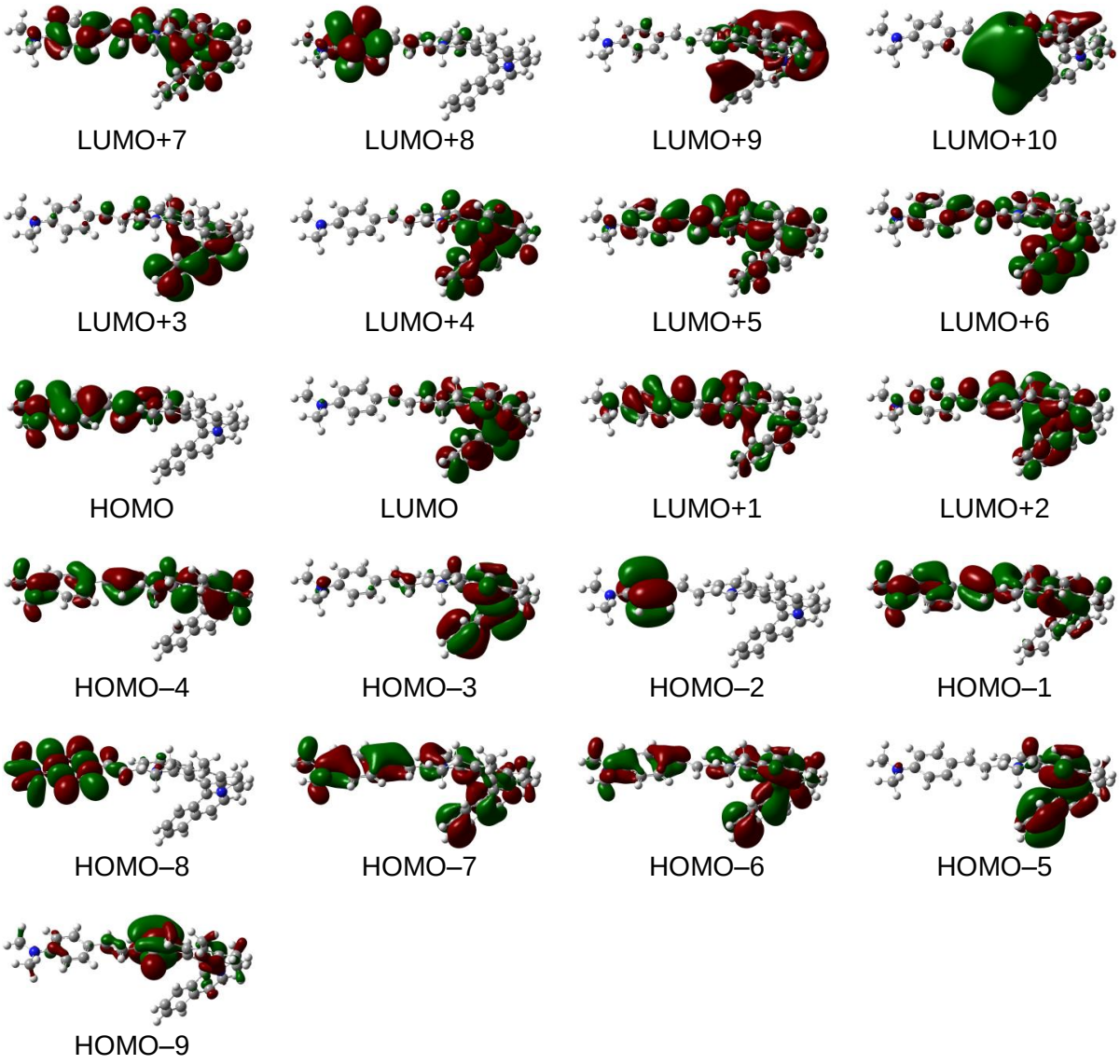



**Fig. S3.** CAM-B3LYP/6-311G(d)-derived contour surface diagrams of the frontier MOs for cation **6′** (isosurface value 0.03 au).

**Table S1** Selected TD-DFT-calculated data for cations **1′** and **6′**[a]

| cation | $\Delta E$ (eV) | $\lambda$ (nm) | $f_{os}$ | Major contributions |
|---|---|---|---|---|
| **1′** | 2.63 | 472 | 1.479 | H → L (81%), H → L+1 (12%) |
| | 3.52 | 352 | 0.252 | H → L (12%), H → L+1 (76%) |
| | 4.04 | 307 | 0.208 | H–3 → L (24%), H–1 → L (28%), H → L+2 (16%) |
| | 4.11 | 302 | 0.199 | H–3 → L (15%), H–2 → L (50%) |
| | 4.13 | 300 | 0.159 | H–2 → L (23%), H → L+2 (48%) |
| | 4.66 | 266 | 0.023 | H–3 → L (24%), H–1 → L (44%), H–1 → L+1 (13%) |
| | 4.70 | 264 | 0.037 | H–3 → L+1 (17%), H–2 → L+1 (18%), H → L+2 (10%), H → L+3 (18%) |
| | 4.86 | 255 | 0.129 | H–3 → L+1 (10%), H–1 → L+1 (12%), H → L+3 (33%), H → L+4 (11%) |
| | 4.90 | 253 | 0.050 | H–4 → L (27%), H → L+3 (12%), H → L+4 (25%), H → L+5 (13%) |
| | 5.08 | 244 | 0.013 | H–3 → L+2 (10%), H–2 → L+1 (55%) |
| | 5.08 | 244 | 0.062 | H–4 → L (15%), H → L+4 (25%), H → L+6 (38%) |
| | 5.21 | 238 | 0.022 | H–3 → L+1 (13%), H–3 → L+2 (28%), H–1 → L+2 (18%) |
| | 5.49 | 226 | 0.112 | H–2 → L+2 (31%), H–1 → L+1 (38%) |
| | 5.58 | 222 | 0.060 | H–3 → L+1 (24%), H–2 → L+2 (38%), H–1 → L+1 (11%) |
| | 5.71 | 217 | 0.098 | H → L+5 (35%), H → L+7 (10%) |
| | 5.82 | 213 | 0.032 | H–7 → L (10%), H–3 → L+3 (15%), H → L+5 (14%) |
| | 5.85 | 212 | 0.010 | H–6 → L (10%), H–5 → L (36%) |
| | 5.93 | 209 | 0.101 | H–7 → L (48%) |
| | 6.08 | 204 | 0.028 | H–4 → L (27%), H–4 → L+1 (66%) |
| | 6.14 | 202 | 0.037 | H–8 → L (12%), H–6 → L (22%), H–1 → L+2 (22%) |
| | 6.26 | 198 | 0.188 | H–2 → L+3 (45%) |
| | 6.29 | 197 | 0.011 | H–9 → L (36%), H–9 → L+1 (15%) |
| | 6.29 | 197 | 0.045 | H–9 → L (12%), H–5 → L (11%), H–3 → L+2 (13%) |
| | 6.36 | 195 | 0.337 | H–8 → L (23%), H–8 → L+1 (10%), H–6 → L (14%) |
| | 6.46 | 192 | 0.105 | H–2 → L+3 (14%), H–2 → L+4 (31%), H–2 → L+5 (14%) |
| | 6.46 | 192 | 0.024 | H → L+10 (86%) |
| **6′** | 2.76 | 449 | 1.570 | H → L (43%), H → L+1 (48%) |
| | 3.37 | 368 | 0.136 | H–1 → L (10%), H → L (37%), H → L+1 (38%) |
| | 3.67 | 338 | 0.297 | H–2 → L (28%), H–1 → L (54%) |
| | 3.87 | 320 | 0.055 | H → L+2 (73%) |
| | 4.00 | 310 | 0.069 | H–3 → L (14%), H–2 → L (49%), H–1 → L |

| | | | |
|---|---|---|---|
| | | | (16%) |
| 4.29 | 289 | 0.042 | H–5 → L (35%), H–3 → L (35%) |
| 4.54 | 273 | 0.049 | H–2 → L+1 (24%), H–1 → L+1 (34%) |
| 4.82 | 257 | 0.022 | H → L+3 (72%) |
| 4.90 | 253 | 0.123 | H–3 → L+1 (12%), H–2 → L+2 (20%), H–1 → L+2 (23%) |
| 5.04 | 246 | 0.070 | H–4 → L (15%), H–4 → L+1 (35%), H → L+5 (14%), H → L+6 (23%) |
| 5.12 | 242 | 0.016 | H–1 → L+1 (28%), H–1 → L+2 (21%) |
| 5.23 | 237 | 0.101 | H–5 → L (20%), H–3 → L (21%), H–2 → L+2 (12%) |
| 5.25 | 236 | 0.075 | H → L+4 (11%), H → L+5 (32%), H → L+7 (19%) |
| 5.32 | 233 | 0.169 | H–5 → L+1 (17%), H–3 → L+2 (16%), H–2 → L+2 (17%), H–1 → L+4 (10%) |
| 5.37 | 231 | 0.173 | H–5 → L (10%), H–5 → L+2 (12%), H–3 → L+1 (49%) |
| 5.51 | 225 | 0.491 | H–6 → L (25%), H–5 → L+1 (14%), H–1 → L+3 (19%) |
| 5.58 | 222 | 0.184 | H–1 → L+3 (17%), H → L+4 (30%), H → L+5 (12%) |
| 5.79 | 214 | 0.032 | H–5 → L+1 (27%), H–3 → L+2 (17%), H → L+7 (10%) |
| 5.85 | 212 | 0.027 | H–5 → L+3 (13%), H–2 → L+3 (32%), H–1 → L+3 (14%) |
| 5.93 | 209 | 0.018 | H–3 → L+2 (12%), H–2 → L+3 (10%), H → L+7 (14%) |
| 5.96 | 208 | 0.153 | H–2 → L+4 (10%), H–1 → L+4 (23%) |
| 6.02 | 206 | 0.058 | H–9 → L (16%), H–5 → L+2 (19%) |
| 6.05 | 205 | 0.044 | H–8 → L (11%), H–3 → L+3 (19%), H–2 → L+3 (10%) |
| 6.08 | 204 | 0.183 | H–9 → L (10%), H–8 → L (32%), H–8 → L+1 (12%) |
| 6.14 | 202 | 0.127 | H–2 → L+4 (27%) |
| 6.26 | 198 | 0.065 | H–11 → L (16%), H–7 → L (19%), H–6 → L+2 (11%) |
| 6.26 | 198 | 0.078 | H–6 → L+1 (39%), H–6 → L+2 (16%) |
| 6.36 | 195 | 0.087 | H–12 → L (13%), H–7 → L+1 (12%), H–6 → L+3 (12%) |
| 6.42 | 193 | 0.262 | H–12 → L (19%), H–11 → L (15%), H–6 → L+3 (11%) |
| 6.46 | 192 | 0.015 | H–10 → L (12%), H–10 → L+1 (38%) |
| 6.46 | 192 | 0.030 | H → L+11 (56%), H → L+13 (16%) |
| 6.53 | 190 | 0.015 | H–6 → L+2 (14%) |
| 6.53 | 190 | 0.124 | H–12 → L (13%), H–8 → L+1 (19%) |

[a] Geometry optimizations and TD-DFT calculations used the CAM-B3LYP functional with the 6-311G(d) basis set, and a CPCM MeCN solvent model was included for TD-DFT. Only the main transitions within each absorption band are included. H = HOMO, L = LUMO.

**Table S2** DFT-optimised coordinates for cation **1′**

| atom | *x* | *y* | *z* |
|---|---|---|---|
| C | 2.533861 | 1.198791 | 1.817479 |
| H | 2.622247 | 0.177452 | 2.155571 |
| C | 1.970217 | 2.154825 | 2.63816 |
| H | 1.601718 | 1.877468 | 3.618417 |
| C | 1.897059 | 3.476366 | 2.209011 |
| H | 1.464741 | 4.254738 | 2.823019 |
| C | 2.427228 | 3.791282 | 0.986427 |
| H | 2.443218 | 4.800985 | 0.600081 |
| N | 2.980472 | 2.845646 | 0.197217 |
| C | 3.618174 | 3.245487 | –1.081886 |
| H | 3.685423 | 4.330184 | –1.095172 |
| H | 2.967896 | 2.924045 | –1.897936 |
| C | 4.974963 | 2.580672 | –1.16517 |
| H | 5.442446 | 2.843327 | –2.114973 |
| H | 5.633161 | 2.957733 | –0.375315 |
| C | 4.801427 | 1.090211 | –1.065573 |
| C | 5.688459 | 0.2192 | –1.68463 |
| H | 6.527072 | 0.616062 | –2.245285 |
| C | 5.52595 | –1.144846 | –1.558514 |
| H | 6.250705 | –1.818122 | –2.002255 |
| C | 4.422224 | –1.669048 | –0.893667 |
| C | 4.229687 | –3.154033 | –0.746698 |
| H | 5.195241 | –3.661272 | –0.759994 |
| H | 3.645664 | –3.559395 | –1.579353 |
| C | 3.526117 | –3.434729 | 0.567213 |
| H | 3.312882 | –4.493514 | 0.693759 |
| H | 4.130961 | –3.103578 | 1.414807 |
| N | 2.242793 | –2.710298 | 0.572722 |
| C | 1.096456 | –3.338976 | 0.941989 |
| H | 1.21548 | –4.34607 | 1.318333 |
| C | –0.121723 | –2.754546 | 0.836277 |
| H | –0.983116 | –3.32679 | 1.148638 |
| C | –0.252354 | –1.44925 | 0.285145 |
| C | 0.974919 | –0.822206 | –0.062308 |
| H | 0.942811 | 0.161568 | –0.510865 |
| C | 2.193648 | –1.425289 | 0.100615 |
| C | 3.473438 | –0.811032 | –0.332009 |
| C | 3.722992 | 0.583087 | –0.329872 |
| C | 3.026383 | 1.536031 | 0.559691 |
| C | –1.477334 | –0.786018 | 0.055659 |
| H | –1.411829 | 0.197529 | –0.397028 |
| C | –2.71574 | –1.312917 | 0.336837 |
| H | –2.747832 | –2.298666 | 0.79356 |

| | | | |
|---|---|---|---|
| C | –3.988227 | –0.747925 | 0.104291 |
| C | –5.142511 | –1.476365 | 0.478459 |
| H | –5.021578 | –2.447912 | 0.946568 |
| C | –6.405449 | –1.003477 | 0.269961 |
| H | –7.24811 | –1.606135 | 0.574804 |
| C | –6.613612 | 0.261363 | –0.345509 |
| C | –5.454632 | 1.003826 | –0.722635 |
| H | –5.563695 | 1.969055 | –1.195108 |
| C | –4.202088 | 0.512931 | –0.503949 |
| H | –3.35558 | 1.113239 | –0.816802 |
| N | –7.849353 | 0.73803 | –0.566457 |
| C | –9.022282 | –0.037781 | –0.17848 |
| H | –9.054766 | –0.99623 | –0.70105 |
| H | –9.918953 | 0.516018 | –0.437739 |
| H | –9.038615 | –0.220466 | 0.898038 |
| C | –8.045223 | 2.032461 | –1.208211 |
| H | –7.604145 | 2.839642 | –0.619152 |
| H | –9.108845 | 2.228426 | –1.298887 |
| H | –7.614154 | 2.048467 | –2.211655 |

**Table S3** DFT-optimised coordinates for cation **6′**

| atom | *x* | *y* | *z* |
|---|---|---|---|
| N | 8.938623 | 0.17543 | –0.569128 |
| C | –1.467294 | –0.645551 | 1.835076 |
| H | –2.475991 | –0.830667 | 2.173323 |
| C | –0.389445 | –1.339288 | 2.401899 |
| H | –0.568716 | –2.079859 | 3.172115 |
| C | 0.87875 | –1.108696 | 1.958783 |
| H | 1.701071 | –1.697778 | 2.3369 |
| C | 1.14195 | –0.129418 | 0.975948 |
| N | 0.061826 | 0.591662 | 0.517569 |
| C | 0.269922 | 1.798879 | –0.30703 |
| H | 0.152943 | 1.54192 | –1.363423 |
| H | 1.288891 | 2.135343 | –0.147571 |
| C | –0.693994 | 2.896799 | 0.1012 |
| H | –0.460887 | 3.239683 | 1.115219 |
| H | –0.519047 | 3.743266 | –0.561647 |
| C | –2.117585 | 2.421636 | 0.002491 |
| C | –3.177903 | 3.280825 | –0.310579 |
| C | –4.479914 | 2.769816 | –0.393714 |
| C | –4.698626 | 1.40977 | –0.162021 |
| C | –6.084138 | 0.824974 | –0.050543 |
| H | –6.788663 | 1.576447 | 0.30291 |
| H | –6.464019 | 0.4605 | –1.010993 |
| C | –6.048416 | –0.299107 | 0.965745 |

| | | | |
|---|---|---|---|
| H | –5.724544 | 0.063711 | 1.9437 |
| H | –7.016458 | –0.780784 | 1.076713 |
| N | –5.089417 | –1.325069 | 0.498947 |
| C | –5.452478 | –2.64582 | 0.559874 |
| H | –6.401234 | –2.850537 | 1.034067 |
| C | –4.652664 | –3.607297 | 0.052937 |
| H | –4.947374 | –4.645841 | 0.131248 |
| C | –3.474 | –3.242358 | –0.640819 |
| C | –2.678155 | –4.20488 | –1.296248 |
| H | –2.945761 | –5.251849 | –1.21663 |
| C | –1.60634 | –3.814294 | –2.048495 |
| H | –1.00767 | –4.554577 | –2.565512 |
| C | –1.297992 | –2.445379 | –2.189819 |
| H | –0.483378 | –2.148636 | –2.839268 |
| C | –2.029658 | –1.494269 | –1.538114 |
| H | –1.806993 | –0.44824 | –1.690834 |
| C | –3.12434 | –1.866201 | –0.717962 |
| C | –3.926166 | –0.91204 | –0.027005 |
| C | –3.626714 | 0.533986 | 0.05583 |
| C | –2.333625 | 1.066218 | 0.241808 |
| C | –1.235647 | 0.290916 | 0.865082 |
| C | 2.439561 | 0.107062 | 0.443156 |
| H | 2.512098 | 0.604147 | –0.513734 |
| C | 3.596725 | –0.284889 | 1.067595 |
| H | 3.509927 | –0.726301 | 2.056945 |
| C | 4.928874 | –0.153122 | 0.609533 |
| C | 5.987392 | –0.565757 | 1.450524 |
| H | 5.75365 | –0.975732 | 2.427868 |
| C | 7.298165 | –0.464695 | 1.080024 |
| H | 8.06357 | –0.795478 | 1.766423 |
| C | 7.65407 | 0.067202 | –0.188523 |
| C | 6.591031 | 0.481411 | –1.044182 |
| H | 6.811342 | 0.88763 | –2.020585 |
| C | 5.289038 | 0.373502 | –0.653016 |
| H | 4.521147 | 0.700124 | –1.345289 |
| C | 10.011352 | –0.252936 | 0.320558 |
| H | 10.002561 | 0.313043 | 1.254694 |
| H | 10.967402 | –0.083373 | –0.164524 |
| H | 9.935049 | –1.317778 | 0.551675 |
| C | 9.284704 | 0.720924 | –1.875658 |
| H | 8.866968 | 0.116057 | –2.683723 |
| H | 10.364463 | 0.724823 | –1.986064 |
| H | 8.932837 | 1.749311 | –1.984422 |
| C | –2.934583 | 4.752804 | –0.507418 |
| H | –2.047658 | 5.099899 | 0.018031 |
| H | –3.769387 | 5.347548 | –0.141869 |

| | | | |
|---|---|---|---|
| H | –2.807795 | 4.996233 | –1.566974 |
| C | –5.629666 | 3.680117 | –0.73665 |
| H | –6.480862 | 3.13746 | –1.142014 |
| H | –5.340337 | 4.413096 | –1.488114 |
| H | –5.977508 | 4.237997 | 0.138027 |

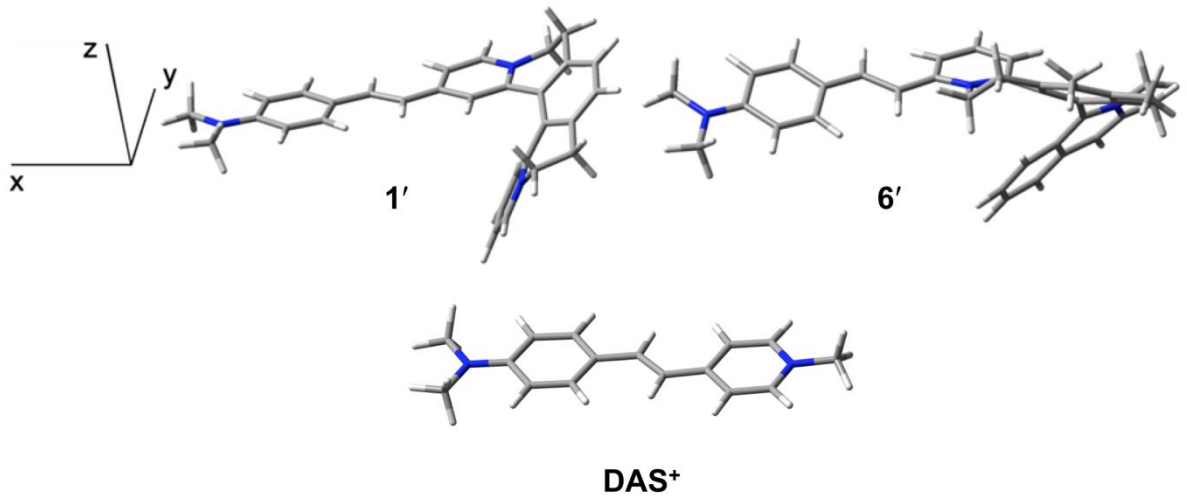



**Fig. S4.** Optimised structures of the cations **1′**, **6′** and $DAS^+$, with the axis convention used in the hyperpolarizability calculations.

**Table S4** Static first hyperpolarizabilities ($10^{-30}$ esu) calculated for the cation **1′** with different functionals[a]

| Functional | $\beta_{xxx}$ | $\beta_{xxy}$ | $\beta_{xyy}$ | $\beta_{yyy}$ | $\beta_{xxz}$ | $\beta_{xyz}$ | $\beta_{yyz}$ | $\beta_{xzz}$ | $\beta_{yzz}$ | $\beta_{zzz}$ | $\beta_{x}$ | $\beta_{y}$ | $\beta_{z}$ | $\beta_{tot}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CAM-B3LYP[a] | 235.6 | –45.7 | 9.7 | 3.9 | 29.6 | –1.5 | 2.2 | 1.3 | 1.8 | 1.2 | 246.6 | –39.9 | 32.9 | 252 |
| B3LYP[a] | 398.9 | 27.0 | 26.0 | 11.5 | 44.9 | 8.0 | 5.6 | 4.1 | 3.5 | 2.1 | 429.1 | 42.1 | 52.6 | 434 |
| M06[a] | 392.2 | 23.8 | 24.7 | 10.9 | 43.0 | 7.2 | 5.3 | 3.9 | 2.0 | 0.0 | 420.8 | 36.7 | 48.3 | 425 |
| CAM-B3LYP[b] | 582.9 | –180.4 | 32.5 | 2.4 | 72.3 | –11.3 | 4.1 | 0.6 | 2.8 | 2.1 | 616.1 | –175.2 | 78.5 | 645 |
| B3LYP[b] | 716.7 | –171.0 | 33.7 | 6.8 | 86.8 | –8.6 | 6.0 | 1.7 | 4.2 | 3.5 | 752.1 | –160.0 | 96.3 | 775 |
| M06[b] | 695.1 | –167.0 | 32.7 | 7.0 | 84.3 | –8.9 | 6.0 | 1.8 | 3.9 | 3.4 | 729.6 | –156.0 | 93.7 | 752 |

All calculations used the 6-311G(d) basis set. [a] In the gas phase. [b] In MeCN.

## 5) References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